

# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : KANEGAFUCHI CHEM IND CO LTD

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(72)Inventor : HASEGAWA NOBUHIRO  
NAKAGAWA YOSHIKI

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## (54) CURABLE COMPOSITION

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a curable composition which has low viscosity and good workability and of which the cured product has diminution in contamination (including paint staining) by suppressing plasticizer bleeding to the surface of the cured product obtained from the curable composition, has a low modulus and a high elongation, maintains its mechanical properties for a long time and has good adhesion and a high gel fraction.

**SOLUTION:** The curable composition is composed of a vinyl-based polymer having at least one crosslinkable silyl group and a polyether-based polymer having on the average 1.2 or below of crosslinkable silyl groups.

were shown in Table 2.

[0228]

[Table 2]

	配合体 ①	粘度 (Pa・s)				柔軟性 材料グッド
		1rpm	2rpm	10rpm	100rpm	
実施例 1.7	P11	2500	1470	480	○	○
実施例 1.8	P11	P15	2680	1560	510	○

柔軟性: ○…良好, ×…不良 (ゆたない…硬シ 3分用シ・カトとして不測)

材料グッド: 良好 → ○ > △ > × → 不良 (バツ)

(Working example 19) [P10] 50 copy obtained in the example 4 of manufacture, and [P15] 40 copy obtained in the example 9 of manufacture to 100 copies which mixed [P17] 50 copy obtained in the example 11 of manufacture, 150 copies of colloid calcium carbonate (Hakuenka CCR: product made from Shiroishi calcium), 20 copies of heavy calcium carbonate (NANOKKUSU 25A: made by Maruo Calcium), Ten copies of titanium oxide (TIPAQUE R-820 (rutile type): made by Ishihara Sangyo), thixotropy grant agent (made in DISUPARON 6500 Kusumoto Chemicals) 2 copy, and an antiaging agent (SANORU LS-765(HALS):Sankyo make.) made in Tinuvin 213:Tiba Specialty Chemicals --- one copy each, [ add and ] After mixing enough with a planetary mixer, one copy each of silanol content compound (A-1120, A-171: all Nippon Unicar make) and two copies of curing catalysts (made in transformation [ U-220 (dibutyl tin diacetyl acetato): Day the east ]) were added further, and the hardenability constituent was produced. Carried out coating of the hardenability constituent to the sheet shaped of about 2-mm thickness like working example 1-18, it was made to harden at a room temperature, and the pliability of the hardened material after settling the hardened material for one week at a room temperature further was evaluated. After settling the hardened material for one week under 30 \*\* x 80% of atmosphere, the surface state of the hardened material was observed. The result was shown in Table 3.

(Working example 20) [P10] 50 copy obtained in the example 4 of manufacture, and [P16] 70 copy obtained in the example 10 of manufacture to 100 copies which mixed [P17] 50 copy obtained in the example 11 of manufacture, 150 copies of colloid calcium carbonate (Hakuenka CCR: product made from Shiroishi calcium), 20 copies of heavy calcium carbonate (NANOKKUSU 25A: made by Maruo Calcium), Ten copies of titanium oxide (TIPAQUE R-820 (rutile type): made by Ishihara Sangyo), thixotropy grant agent (made in DISUPARON 6500 Kusumoto Chemicals) 2 copy, and an antiaging agent (SANORU LS-765(HALS):Sankyo make.) made in Tinuvin 213:Tiba Specialty Chemicals --- one copy each, [ add and ] After mixing enough with a planetary mixer, one copy each of silanol content compound (A-1120, A-171: all Nippon Unicar make) and two copies of curing catalysts (made in transformation [ U-220 (dibutyl tin diacetyl acetato): Day the east ]) were added further, and the hardenability constituent was produced. Carried out coating of the hardenability constituent to the sheet shaped of about 2-mm thickness like working example 1-18, it was made to harden at a room temperature, and the pliability of the hardened material after settling the hardened material for one week at a room temperature further was evaluated. After settling the hardened material for one week under 30 \*\* x 80% of atmosphere, the surface state of the hardened material was observed. The result was shown in Table 3.

(Working example 21) [P12] 70 copy obtained in the example 6 of manufacture, and [P15] 40 copy obtained in the example 9 of manufacture to 100 copies which mixed [P17] 30 copy obtained in the example 11 of manufacture, 150 copies of colloid calcium carbonate (Hakuenka CCR: product made from Shiroishi calcium), 20 copies of heavy calcium carbonate (NANOKKUSU 25A: made by Maruo Calcium), Ten copies of titanium oxide (TIPAQUE R-820 (rutile type): made by Ishihara Sangyo), thixotropy grant agent (made in DISUPARON 6500 Kusumoto Chemicals) 2 copy, and an antiaging agent (SANORU LS-765(HALS):Sankyo make.) made in Tinuvin 213:Tiba Specialty Chemicals --- one copy each, [ add and ] After mixing enough with a planetary mixer, one copy each of silanol content compound (A-1120, A-171: all Nippon Unicar make) and two copies of curing catalysts (made in transformation [ U-220 (dibutyl tin diacetyl acetato): Day the east ]) were added further, and the hardenability constituent was produced. Carried out coating of the hardenability constituent to the sheet shaped of about 2-mm thickness like working example 1-18, it was made to harden at a room temperature, and the pliability of the hardened material after settling the hardened material for one

week at a room temperature further was evaluated. After settling the hardened material for one week under 30 \*\* x 80% of atmosphere, the surface state of the hardened material was observed. The result was shown in Table 3.

(Working example 22) [P12] 70 copy obtained in the example 6 of manufacture, and [P16] 70 copy obtained in the example 10 of manufacture to 100 copies which mixed [P17] 30 copy obtained in the example 11 of manufacture, 150 copies of colloid calcium carbonate (Hakuenka CCR: product made from Shiroishi calcium), 20 copies of heavy calcium carbonate (NANOKKUSU 25A: made by Maruo Calcium), Ten copies of titanium oxide (TIPAQUE R-820 (rutile type): made by Ishihara Sangyo), thixotropy grant agent (made in DISUPARON 6500 Kusumoto Chemicals) 2 copy, and an antiaging agent (SANORU LS-765(HALS):Sankyo make.) made in Tinuvin 213:Tiba Specialty Chemicals --- one copy each, [ add and ] After mixing enough with a planetary mixer, one copy each of silanol content compound (A-1120, A-171: all Nippon Unicar make) and two copies of curing catalysts (made in transformation [ U-220 (dibutyl tin diacetyl acetato): Day the east ]) were added further, and the hardenability constituent was produced. Carried out coating of the hardenability constituent to the sheet shaped of about 2-mm thickness like working example 1-18, it was made to harden at a room temperature, and the pliability of the hardened material after settling the hardened material for one week at a room temperature further was evaluated. After settling the hardened material for one week under 30 \*\* x 80% of atmosphere, the surface state of the hardened material was observed. The result was shown in Table 3.

[0229]

[Table 3]

	重合体					材料グッド
	P10	P12	P17	P15	P16	
実施例 1.9	50	—	50	40	—	○
実施例 2.0	50	—	50	—	70	○
実施例 2.1	—	70	30	40	—	○
実施例 2.2	—	50	40	—	60	○

柔軟性: ○…良好, ×…不良 (ゆたない…硬シ 3分用シ・カトとして不測)

材料グッド: 良好 → ○ > △ > × → 不良 (バツ)

Each hardenability constituent using the polyether system polymer which averages with the vinyl-base polymer which has at least one crosslinkable silyl groups, and has 1.2 or less crosslinkable silyl groups showed good viscosity and pliability. Oil bleeding was also good.

[0230]

[Effect of the Invention]The vinyl-base polymer in which this invention has at least one crosslinkable silyl groups, And it consists of a hardenability constituent which consists of a polyether system polymer which has 1.2 or less crosslinkable silyl groups on the average, When the viscosity of a hardenability constituent controls the bleeding of the plasticizer to the surface of the hardened material which has low good workability and stiffened the hardenability constituent, contamination (paint stain resistance is included) of a hardened material is reduced, and the hardened material is a low modulus and high elongation.

And the mechanical physical property is maintained over a long period of time, and the constituent which has still better alkyl paintwork and a high gel fraction can be realized.

[Translation done.]

[Claim 16] The hardenability constituent according to claim 15, wherein a metal complex made into a catalyst contains a vinyl-base polymer which is a complex chosen from a group which consists of a complex of copper, nickel, a ruthenium, or iron.  
[Claim 17] The hardenability constituent according to claim 16, wherein a metal complex made into a catalyst contains a vinyl-base polymer which is a copper complex.

[Translation done.]

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CLAIMS

[Claim(s)]  
[Claim 1] The following two ingredients: Vinyl-base polymer (I) which has at least one crosslinkable silyl groups, and a hardenability constituent containing polyether system polymer (II) which has 1.2 or less crosslinkable silyl groups on the average.  
[Claim 2] The hardenability constituent according to claim 1, wherein crosslinkable silyl groups of polyether system polymer (II) is in a main chain terminal.  
[Claim 3] The hardenability constituent according to claim 2, wherein crosslinkable silyl groups of polyether system polymer (II) has only at the one end in a main chain and does not have in other ends.  
[Claim 4] It is a hardenability constituent given in any 1 paragraph among Claims 1-3, wherein molecular weight distribution contains vinyl-base polymer (I) which is less than 1.8.  
[Claim 5] A main chain An acrylic system monomer (meta), an acrylonitrile series monomer, it is a hardenability constituent given in any 1 paragraph among Claims 1-4 containing vinyl-base polymer (I) which is what mainly polymerizes and is manufactured in a monomer chosen from a group which consists of an aromatic vinyl system monomer, a fluoride content vinyl system monomer, and a silicon content vinyl system monomer.  
[Claim 6] The hardenability constituent according to claim 5, wherein a main chain contains vinyl-base polymer (I) which is an acrylic (meta) polymer.  
[Claim 7] The hardenability constituent according to claim 6, wherein a main chain contains vinyl-base polymer (I) which is an acrylic polymer.  
[Claim 8] The hardenability constituent according to claim 7, wherein a main chain contains vinyl-base polymer (I) which is an acrylic ester system polymer.  
[Claim 9] The hardenability constituent according to claim 8, wherein a main chain contains vinyl-base polymer (I) which is a butyl acrylate system polymer.  
[Claim 10] It is a hardenability constituent given in any 1 paragraph to vinyl-base polymer (I) 100 weight section among Claims 1-9 carrying out 5-100 weight-section content of polyether system polymer (II).  
[Claim 11] It is a hardenability constituent given in any 1 paragraph among Claims 1-10 containing polyether system polymer (III) which has at least 1.2 or more cross-linking functional groups as the third component.  
[Claim 12] Ten to polyether system polymer (I) 50 weight section which has 1.2 or less crosslinkable silyl groups on the average to vinyl-base polymer (I) 100 weight section, The hardenability constituent containing polyether system polymer (III) which has at least 1.2 or more cross-linking functional groups according to claim 11.  
[Claim 13] It is a hardenability constituent given in any 1 paragraph among Claims 1-12, wherein a main chain of vinyl-base polymer (I) contains a vinyl-base polymer which is what is manufactured by a living-radical-polymerization method.  
[Claim 14] The hardenability constituent according to claim 13, wherein living radical polymerization contains a vinyl-base polymer which is atom transfer radical polymerization.  
[Claim 15] The hardenability constituent according to claim 14 in which atom transfer radical polymerization is characterized by containing a vinyl-base polymer in which a complex chosen from a transition metal complex which uses the 7th fellows of the periodic table, eight fellows, nine fellows, ten fellows, or 11 group elements as a central metal is made into a catalyst.

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to vinyl-base polymer (I) which has at least one crosslinkable silyl groups, and the hardenability constituent containing polyether system polymer (II) which has 1.2 or less crosslinkable silyl groups on the average.

[0002]

[Description of the Prior Art] What has a functional group at a functional group, especially the end with the polymer of a vinyl system obtained by a radical polymerization by one side of the polymer obtained by ionic polymerization or condensation polymerization has hardly been put in practical use yet. Also in the vinyl-base polymer, the acrylic (meta) polymer has the characteristics which are not obtained in a polyether system polymer, a hydrocarbon system polymer, or a polyester system polymer, such as high weatherability and transparency.

What has an alkenyl group and crosslinkable silyl groups in a side chain is used for the high weatherability paint etc.

On the other hand, the polymerization control of an acrylic polymer is not easy because of the side reaction, and introduction of the functional group to an end is dramatically difficult.

[0003] If the vinyl-base polymer which has an alkenyl group in molecular chain terminals can be obtained by a simple method, the hardened material which excelled [side chain] in hardened material physical properties as compared with what has a cross-linking group can be obtained. Therefore, although the manufacturing method has been examined by the researcher of the former many, it is not easy to manufacture them industrially. For example, the synthetic method of the acrylic polymer which has an alkenyl group at the end (meta) which uses alkenyl group content disulfide as a chain transfer agent is indicated by JP,H1-247403,A and JP,H5-255415,A.

[0004] In JP,H5-262808,A, the vinyl-base polymer which has hydroxyl in both ends is compounded using the disulfide which has hydroxyl, and the synthetic method of the acrylic polymer which has an alkenyl group at the end (meta) is further indicated using the reactivity of hydroxyl.

[0005] In JP,H5-211922,A, the vinyl-base polymer which has hydroxyl in both ends is compounded using the polysulfide which has hydroxyl, and the synthetic method of the acrylic polymer which has a silyl group at the end (meta) is further indicated using the reactivity of hydroxyl.

[0006] In these methods, it is difficult to introduce a functional group into both ends certainly, and the hardened material which has the satisfactory characteristic cannot be obtained. In order to introduce a functional group into both ends certainly, a chain transfer agent must be used in large quantities, and it is a manufacturing process top problem. Since the usual radical polymerization is used by these methods, the molecular weight of the polymer obtained and control of molecular weight distribution (ratio of a number average molecular weight to a number average molecular weight) are difficult.

[0007] The vinyl-base polymer in which artificers have various cross-linking functional groups at the end to such a Prior art until now, The manufacturing method, a hardenability constituent, Concerning [and ] a use. Much inventions. Have carried out. JP,11-080249,A, JP,11-080250,A, JP,11-05815,A, JP,11-116817,A, JP,11-116806,A, JP,11-080571,A, JP,11-080570,A, JP,11-130931,A, and JP,11-100433,A. Refer to JP,11-116763,A, JP,H9-272714,A, JP,H9-272715,A, etc.

[0008] For example, the silicon content group which can construct a bridge by having the hydroxyl group or hydrolytic basis combined with the silicon atom, and forming a siloxane bond with hygroscopic surface moisture etc. also in a room temperature. The vinyl-base polymer which has (it

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is also hereafter called "crosslinkable silyl groups"), or the hardened material obtained from the constituent. Although it excels in heat resistance or weatherability and limitation in particular is not carried out, sealing materials, such as structural elastic sealing compound sealant and a sealing material for multiple glass. Electrocal insulation materials, such as electric electronic component materials, such as a solar cell rear-face sealing agent, pre-insulation an electric wire, material for cables, A binder, adhesives, elastic adhesives, a paint, powder coatings, a coating material, foam, it is available for a use with various seals, such as the potting agent for electric electrons, a film, a gasket, casting material, various molding materials and wired sheet glass and the sealing agent for rust prevention / water proof of the glass laminate end face (cut section), autoparts, electrical machinery parts, several kinds of machine part, etc.

[0009] Also in the aforementioned use, the joined part and crevice between various members are generally filled up with a sealing material, especially general structural sealant, etc., and they are used in order to give watertight and airtightness. Therefore, since the flattery nature to the use part over a long period of time is very important, being a low modulus, high elongation, and high intensity, and holding those physical properties as physical properties of a hardened material, over a long period of time is called for. By one side, hypoviscosity is demanded as a hardenability constituent (compound) in consideration of workability in these construction.

[0010] The hardened material of the hardenability constituent which made it the raw material when Polymer Division quantification of the vinyl-base polymer was carried out --- a low modulus and high elongation --- although it can high-intensity-size, the viscosity of this compound becomes high and the workability at the time of construction worsens. On the contrary, if a vinyl-base polymer is hypoviscosity-sized, although workability becomes good, the mechanical physical property of a hardened material will fall (a high modulus, low elongation, low-strength-izing). Then, in order to solve this SUBJECT, a phthalate system plasticizer usually like the phthalic ester which does not have a functional group, a polyether system plasticizer, etc. are used.

[0011]

[Problem(s) to be Solved by the Invention] However, if such a plasticizer is blended so much, in the hardened material which stiffened the compound, a plasticizer will pass, bleeding (it is also called shift as oil bleeding) will be carried out to the hardened material surface by the time, and problems, such as smeariness, will be produced. The problem of causing the contamination to the circumference of hardened materials (sealant etc.), the surface contamination after paint, an adhesive fall, and the fall of the hardness of a hardened material, elongation, etc. by that is also produced.

[0012] Since the polymer which has a hydrolytic silicon group which two adding-water nature resolvability groups per silicon atom combine was used in many cases, the vinyl-base polymer which has such crosslinkable silyl groups. To take [when you need the very quick especially cure rates in the case of using it at the use etc. and low temperature of adhesives, etc. the cure rate is not enough, and ] out the pliability after hardening. Crosslinking density needed to be reduced, therefore since crosslinking density was not enough, there was a problem that there was stickiness (surface tackiness).

[0013] Then, the vinyl-base polymer in which this invention has at least one crosslinkable silyl groups, And it is a hardenability constituent which uses as the main ingredients the polyether system polymer which has 1.2 or less crosslinkable silyl groups on the average, Have good workability by hypoviscosity and contamination (paint stain resistance is included) of a hardened material is reduced by controlling the bleeding of the plasticizer to the surface of the hardened material which stiffened the hardenability constituent. The hardened material is a low modulus and high elongation, and the mechanical physical property is maintained over a long period of time, and it is in providing the constituent which reveals still better adhesive and good alkyl paintwork and a high gel fraction.

[0014]

[Means for Solving the Problem] A result wholeheartedly examined in order that this invention persons might solve such a problem. By using a vinyl-base polymer which has at least one crosslinkable silyl groups, and a hardenability constituent which uses as the main ingredients a polyether system polymer which has 1.2 or less crosslinkable silyl groups on the average, it found out solving an aforementioned problem and this invention was completed.

[0015] That is, this invention relates to vinyl-base polymer (I) which has at least one crosslinkable silyl groups, and a hardenability constituent containing polyether system polymer (II) which has 1.2 or

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less crosslinkable silyl groups on the average.

[0016]Although vinyl-base polymer (I) in particular is not limited, it is preferred that a value of a ratio (Mw/Mn) of weight average molecular weight (Mw) and a number average molecular weight (Mn) which were measured with gel permeation chromatography is less than 1.8.

[0017]Although a main chain in particular of vinyl-base polymer (I) is not limited, an acrylic system monomer (meta), it is preferred to mainly polymerize and to manufacture a monomer chosen from a group which consists of an acrylonitrile series monomer, an aromatic vinyl system monomer, a fluoride content vinyl system monomer, and a silicon content vinyl system monomer, more — desirable — an acrylic system monomer (meta-) — further — desirable — an acrylic system monomer. It is an acrylic ester system monomer more preferably, and it is most preferred to be polymerized and manufactured using a butyl acrylate system monomer from a point that physical properties, such as hypoviscosity of a compound, a low modulus of a hardened material, high elongation, weatherability, and heat resistance, are required in a use of general \*\*\*\*\*. In a use of the circumference of an engine of a car of which oil resistance, heat resistance, high intensity, etc. are required by one side, machinery, etc., it is preferred to be polymerized and manufactured using an ethyl acrylate system monomer, and also it is more preferred to carry out copolymerization of the ethyl acrylate system monomer mainly using an acrylic acid 2-methoxy ethyl system monomer and a butyl acrylate system monomer, and to be manufactured from balance, such as cold resistance. It is possible to change a ratio of a monomer which carries out copolymerization in consideration of physical properties, such as oil resistance and the low-temperature characteristic.

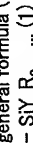
[0018]Although limitation is not carried out, as for a main chain of this vinyl-base polymer (I), being manufactured by living radical polymerization is preferred, and it is more preferred that it is atom transfer radical polymerization. Although limitation is not carried out, atom transfer radical polymerization The 7th fellows of the periodic table. It is preferred to make into a catalyst a complex chosen from a transition metal complex which uses eight fellows, nine fellows, ten fellows, or 11 group elements as a central metal, a complex chosen from a group which consists of a complex of copper, nickel, a ruthenium, or iron is more preferred, and especially a copper complex is especially preferred.

[0019]A position of crosslinkable silyl groups of vinyl-base polymer (I) has a preferred end, although limitation is not carried out. In addition, although you may have a functional group of Mr. inside \*\*\*\* of a main chain, when asking for rubber elasticity a hardened material made to construct a bridge, it is preferred to have a functional group only at the end.

[0020]Although the number in particular of cross-linking functional groups of vinyl-base polymer (I) is not limited, in order to obtain a hardened material with higher cross-linking, it is preferred to have one or more pieces on the average, and it is 1.2 or more pieces [ 3.5 or less ] still more preferably 4.0 or less [ 1.1 or more ] more preferably.

[0021]As for polyether system polymer (II) which averages and has 1.2 or less crosslinkable silyl groups, although limitation in particular is not carried out, it is preferred that crosslinkable silyl groups is in a main chain terminal. Although what it has only at the one end in a main chain, and does not have in other ends is preferred as for crosslinkable silyl groups of this polyether system polymer (II), it averages, and it will not be limited especially if it is 1.2 or less pieces.

[0022]On the other hand, it is preferred that vinyl-base polymer (I) contains a vinyl-base polymer which is the crosslinkable silyl groups whose a is 3 among crosslinkable silyl groups expressed with a general formula (1) in order to raise a cure rate and crosslinking density of a compound.



however, the inside R of a formula — an alkyl group of the carbon numbers 1-20, and an aryl group of the carbon numbers 6-20. An aralkyl group or (R')<sub>3</sub>SiO of the carbon numbers 7-20 — (R' is a univalent hydrocarbon group of the carbon numbers 1-20, and) three R' being the same and differing — \*\*\*\* — when the TORI ORGANO siloxy group shown is shown and two or more R exists, they may be the same and may differ. When Y shows a hydroxyl group or a hydrolytic basis and two or more Y exists, they may be the same and may differ. a shows 1, 2, or 3.

As mentioned above, a position of crosslinkable silyl groups expressed with this formula (1) has a preferred main chain terminal of vinyl-base polymer (I), although limitation is not carried out.

[0023]

[Embodiment of the Invention]This invention relates to a hardenability constituent. It is related with

vinyl-base polymer (I) which has following at least one two ingredient-cross-linking functional group, and the hardenability constituent containing polyether system polymer (II) which has 1.2 or less crosslinkable silyl groups on the average in detail. Below, the hardenability constituent of this invention is explained in full detail.

< <vinyl-base polymer> > <main chain> this invention persons, The vinyl-base polymer which has various cross-linking functional groups in a polymer terminal until now, The manufacturing method, a hardenability constituent, Concerning [ and ] a use. Much inventions. Have carried out. JP,11-080249,A, JP,11-080250,A, JP,11-005815,A, JP,11-116617,A, JP,11-116606,A, JP,11-080571,A, JP,11-080570,A, JP,11-1130931,A, and JP,11-100433,A. Refer to JP,11-116763,A, JP,H9-272714,A, JP,H9-272715,A, etc. Although not limited especially as vinyl-base polymer (I) of this invention, all the polymers indicated by the invention illustrated above can be used conveniently.

[0024]Especially, as a vinyl system monomer which constitutes the main chain of the vinyl-base polymer of this invention, it is not limited but various kinds of things can be used. If it illustrates, acrylic acid (meta), methyl acrylate (meta), (Meta) Ethyl acrylate, acrylic acid (meta)-n-propyl, acrylic acid (meta) isopropyl, (Meta) Acrylic acid-n-butyl, isobutyl acrylate (meta), (Meta) Acrylic acid-tert-butyl, acrylic acid (meta)-n-pentyl, (Meta) Acrylic acid-n-hexyl, acrylic acid (meta) cyclohexyl, (Meta) Acrylic acid-n-heptyl, acrylic acid (meta)-n-octyl, (Meta) Acrylic acid-2-ethylhexyl, cyclohexyl, acrylic acid (meta) nonyl, (Meta) Decyl acrylate, acrylic acid (meta) dodecyl, acrylic acid (meta) phenyl, (Meta) Acrylic acid tolyl, acrylic acid (meta) benzyl, acrylic acid (meta)-2-methoxy ethyl, (Meta) Acrylic acid-3-methoxy butyl, acrylic acid (meta)-2-hydroxyethyl, (Meta) Acrylic acid-2-hydroxypropyl, acrylic acid (meta) stearyl, metaglycidyl acrylate (meta), acrylic acid (meta) 2-aminoethyl, gamma-(methacryloyl oxypropyl) trimethoxysilane, the ethyleneoxide addition of acrylic acid (meta), (Meta) Acrylic acid trifluoromethyl methyl, an acrylic acid (meta) 2-trifluoro methyl, (Meta) Acrylic acid perfluoro ethyl methyl, acrylic acid (meta) 2-perfluoro ethylethyl, (Meta) Acrylic acid perfluoro ethyl perfluoro BUOHIRUMECHIRU, (Meta) Acrylic acid 2-perfluoro ethyl-2-perfluoro butylethyl, (Meta) Acrylic acid perfluoro ethyl, acrylic acid (meta) perfluoro methyl, (Meta) Acrylic acid JIPA fluoromethylmethyl, an acrylic acid (meta) 2,2-JIPA fluoro methyl, (Meta) Acrylic acid perfluoro methyl perfluoro ECHIRUMECHIRU, (Meta) Acrylic acid 2-perfluoro methyl-2-perfluoro ethylethyl, (Meta) Acrylic acid 2-perfluoro decylmethyl, acrylic acid (meta) 2-perfluoro decylethyl, (Meta) Acrylic acid hexadecylethyl (meta); Styrene, vinyltoluene, Aromatic vinyl system monomers, such as alpha-methylstyrene, KURORU styrene, styrene sulfonic acid, and its salt; Perfluoro ethylene, Fluoride content vinyl system monomers, such as perfluoro propylene and vinylidene fluoride;

Vinyltrimethoxysilane, Silicon content vinyl system monomers, such as vinyltriethoxysilane; A maleic anhydride, Monoalkyl ester and dialkyl ester of maleic acid and maleic acid; Fumaric acid, Monoalkyl ester and dialkyl ester of fumaric acid; Maleimide, Methylmaleimide, ethylmaleimide, propyl maleimide, butylmaleimide, Hexylmaleimide, octylmaleimide, dodecylmaleimide, stearyl maleimide, Maleimide system monomers, such as phenylmaleimide and cyclohexylmaleimide; Acrylonitrile, Acrylonitrile series monomers, such as methacrylonitrile; Acrylamide, Amide group content vinyl system monomers, such as methacrylamide; Vinyl acetate, Conjugated dienes, such as alkenes; butadiene, such as vinyl ester, ethylene, such as vinyl propionate, vinyl pivalate, benzoic acid vinyl, and vinyl cinnamic acid, and propylene, and isoprene; VCM/PVC, a vinylidene chloride, An allyl chloride, allyl alcohol, etc. are mentioned. These may be used independently, and even if it carries out

copolymerization of the plurality, they are not cared about.

[0025]The main chain of a vinyl-base polymer An acrylic system monomer (meta), an acrylonitrile series monomer, It is preferred that it is what mainly polymerizes and is manufactured in at least one monomer chosen from the group which consists of an aromatic vinyl system monomer, a fluoride content vinyl system monomer, and a silicon content vinyl system monomer. "Mainly concerning" means more than 50 mol % and being the above-mentioned monomer not less than 70% of preferably here among the monomeric units which constitute a vinyl-base polymer.

[0026]Especially, the styrene system monomer from physical properties etc. and (meta) acrylic acid series monomer of output are preferred. More preferably, it is acrylic ester monomer and a methacrylic-acid-ester monomer, and is acrylic ester monomer especially preferably. The point that physical properties, such as hypoviscosity of a compound, a low modulus of a hardened material, high

elongation, weatherability, and heat resistance, are required in the use of general \*\*\*\*\* to a butyl acrylate system monomer is still more preferred. The copolymer mainly concerned with ethyl acrylate on the other hand in the use as which oil resistance, such as an automotive application, etc. are required is still more preferred. It can also transpose a part of ethyl acrylate to butyl acrylate in order to raise that low-temperature characteristic, since it tends to be a little inferior to the low-temperature characteristic (cold resistance), although the polymer mainly concerned with this ethyl acrylate is excellent in oil resistance. However, since it follows on increasing the ratio of butyl acrylate and the good oil resistance is spoiled, as for the ratio, for the use of which oil resistance is required, it is preferred to carry out to 40% or less, and also it is more preferred to make it to 30% or less. In order to improve the low-temperature characteristic etc., without spoiling oil resistance, it is also preferred to use acrylic acid 2-methoxy ethyl, acrylic acid 2-ethoxyethyl, etc. by which oxygen was introduced into the alkyl group of the side chain. However, since it is in the tendency for heat resistance to be inferior by introduction of an alkoxy group which has an ether bond in a side chain, when heat resistance is required, it is preferred [the ratio] to make it to 40% or less. It is possible to obtain the polymer which changed the ratio and was suitable in consideration of physical properties needed, such as oil resistance, heat resistance, and the low-temperature characteristic, according to a various application or the purpose demanded. For example, as an example which is excellent in properties balance, such as oil resistance, heat resistance, the low-temperature characteristic, although limitation is not carried out, the copolymer of ethyl acrylate / butyl acrylate / acrylic acid 2-methoxy ethyl (it is 40-50/20-30/30-20 at a weight ratio) is mentioned.

[0027]In this invention, it is preferred other monomers, copolymerization, and also that may carry out block copolymerization and these desirable monomers are contained 40% by the weight ratio in these desirable monomers in that case. Acrylic acid (meta) expresses acrylic acid and/or methacrylic acid with the above-mentioned expressive form.

[0028]The molecular weight distribution of the vinyl-base polymer of this invention, i.e., the ratio of the weight average molecular weight (Mw) and the number average molecular weight (Mn) which were measured with gel permeation chromatography, (Mw/Mn), Although not limited in particular, it is less than 1.8 preferably, is 1.7 or less more preferably, is 1.6 or less still more preferably, is 1.5 or less still more preferably, is 1.4 or less especially preferably, and is 1.3 or less most preferably. In the GPC measurement by this invention, using chloroform as a mobile phase, a polystyrene gel column can perform measurement and number average molecular weights can usually be calculated by polystyrene conversion.

[0029]Although the number average molecular weight of the vinyl-base polymer in this invention does not have restriction in particular, when it measures with gel permeation chromatography, the range of 500-1,000,000 is preferred, 1,000-100,000 are more preferred, and 5,000-50,000 are still more preferred.

Although limitation is not carried out, the synthetic method of a vinyl-base polymer in <synthetic method of main chain> this invention has a preferred control radical polymerization, is more preferred, and is preferred. [of especially atom transfer radical polymerization] [of living radical polymerization] These are explained below.

"A general radical polymerization method" to which copolymerization of the monomer in which a control radical polymerization radical polymerization method has a specific functional group using an azo compound, a peroxide, etc. as a polymerization initiator, and the vinyl system monomer is only carried out. It can classify into the "control radical polymerization method" which can introduce a specific functional group into the position by which the end etc. were controlled.

[0030]Although "a general radical polymerization method" is a simple method. Since the monomer which has a specific functional group by this method is not introduced into a probable polymer, when it is going to obtain a polymer with a high rate of organic-functions-izing, it is necessary to use this monomer quite in large quantities, and there is a problem that the rate of a polymer that this specific functional group is not introduced becomes large, by use in small quantities conversely. Since it is a free radical polymerization, the problem that only a large polymer with high viscosity is obtained also has molecular weight distribution.

[0031]A "chain transfer agent method" by which the vinyl-base polymer which has a functional group at the end when a "control radical polymerization method" polymerizes using the chain transfer agent which has a still more specific functional group is obtained, it can classify into the "living-radical-

polymerization method" the polymer of the molecular weight as a design is obtained mostly, by growing without a polymerization growth end causing a termination reaction etc.

[0032]Although the "chain transfer agent method" can obtain a polymer with a high rate of organic-functions-izing, the chain transfer agent which has quite a lot of specific functional groups to an initiator is required, and there is a problem on the financial side also including processing. Like the above-mentioned "general radical polymerization method", since it is a free radical polymerization, the problem that only the polymer whose viscosity it is large and is high is obtained also has molecular weight distribution.

[0033]Unlike these polymerizing methods, a "living-radical-polymerization method", Since a rate of polymerization is high, and the termination reaction by radical coupling etc. occurs easily, though it is a radical polymerization made difficult [control], While a termination reaction does not occur easily and the narrow (Mw/Mn is 1.1 to about 1.5) polymer of molecular weight distribution is obtained, a molecular weight is freely controllable by the preparation ratio of a monomer and an initiator.

[0034]Therefore, since the monomer which can obtain a polymer with molecular weight distribution narrow [a "living-radical-polymerization method"] and low viscosity, and also has a specific functional group can be introduced into the almost arbitrary positions of a polymer, As a manufacturing method of the vinyl-base polymer which has the above-mentioned specific functional group, it is more desirable.

[0035]Although living polymerization means the polymerization in which an end always continues having activity and the chain grows in the narrow sense, the pseudo-living polymerization which grows while that by which the end was inactivated, and the activated thing are generally in an equilibrium situation is also included. The definition in this invention is also the latter.

[0036]As for the "living-radical-polymerization method", research is positively made into various groups in recent years. As the example, for example A journal OBU American chemical society (J. Am.Chem.Soc.), 1994, 116 volumes, the thing using a cobalt porphyrin complex as shown in 7943 pages, Macro leakage-at-bulb KYURUZU (Macromolecules), 1994, The thing using radical scavengers, such as a nitroxide compound as shown in 27 volumes and 7228 pages, The "atom transfer radical polymerization" (Atom Transfer Radical Polymerization:ATRP) etc. which uses an organic halogenated compound etc. as an initiator and makes a transition metal complex a catalyst is raised.

[0037]Also in a "living-radical-polymerization method", an organic halogenated compound or a sulfonyl halide compound An initiator, The "atom-transfer-radical-polymerization method" which polymerizes a vinyl system monomer by making a transition metal complex into a catalyst, As a manufacturing method of the vinyl-base polymer which in addition to the feature of the above-mentioned "living-radical-polymerization method" has halogen comparatively advantageous to a functional group conversion reaction etc. at the end, and has a specific functional group from the flexibility of a design of an initiator or a catalyst being large, it is still more desirable. As this atom-transfer-radical-polymerization method, Matyjaszewski et al. [for example, J. Journal OBU American chemical society (J. Am.Chem.Soc.) 1995, 117 volumes, 5614 pages, macro leakage-at-bulb KYURUZU (Macromolecules) 1995, 28 volumes, 7901 pages, science (Science) 1996, 272 volumes, 866 pages, WO 96/No. 30421 gazette, WO 97/No. 18247 gazette, 28 volumes, 1721 pages, JP,H9-208816,A, JP,H8-41117,A, etc. will be mentioned in WO 98/No. 01480 gazette, WO 98/No. 40415 gazette or Sawamoto et al., and macro leakage-at-bulb KYURUZU (Macromolecules) 1995.

[0038]In this invention, although which method is used among such living radical polymerization does not have restrictions in particular, an atom-transfer-radical-polymerization method is preferred.

[0039]Although living radical polymerization is explained in detail below, the polymerization using 1 of the control radical polymerizations which can be used for manufacture of the vinyl-base polymer explained later, and a chain transfer agent is explained before that. Especially as a radical polymerization using a chain transfer agent (telomer), although not limited, the following two methods are illustrated as a method of obtaining a vinyl-base polymer with terminal structures suitable for this invention.

[0040]How to obtain the polymer of a halogen end using halogenated hydrocarbon as shown in JP,H4-132706,A as a chain transfer agent, It is the method of obtaining the polymer of a hydroxyl group end using hydroxyl group content mercaptan or hydroxyl group content polysulfide as shown in JP,S61-271306,A, JP,2594402,B, and JP,S54-47782,A etc. as a chain transfer agent.

[0041]Below, living radical polymerization is explained.



[0042] Before long, how to use radical scavengers, such as a nitroxide compound, is explained first. Generally in this polymerization, a stable nit ROKISHI free radical (=N-O-) is used as a radical capping agent. As such compounds, although limitation is not carried out, the nit ROKISHI free radical from annular hydroxyamine, such as a 2,2,6,6-substitution-1-piperidinyloxy radical and a 2,2,5,5-substitution-1-pyrrolidinyloxy radical, is preferred. As a substituent, a with a carbon numbers [ such as a methyl group and an ethyl group, ] of four or less alkyl group is suitable. As a concrete nit ROKISHI free radical compound, Although limitation is not carried out, 2, 2, 6, a 6-tetramethyl-1-piperidinyloxy radical (TEMPO), A 2, 2, 6, and 6-tetraethyl 1-piperidinyloxy radical, A 2, 2, 6, and 6-tetramethyl 4-oxo 1-piperidinyloxy radical, A 2,2,5,5-tetramethyl 1-pyrrolidinyloxy radical, a 1,1,3,3-tetramethyl 2-iso indri NIRUOKISHI radical, a N,N-di-tert-butylamine oxy radical, etc. are mentioned. Instead of a nit ROKISHI free radical, a free radical with a stable galvinoxyl (galvinoxyl) free radical etc. may be used.

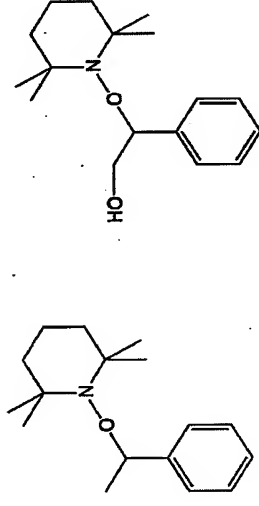
[0043] The above-mentioned radical capping agent is used together with a radical generator. The resultant of a radical capping agent and a radical generator is considered that it becomes a polymerization initiator and the polymerization of an addition condensation nature monomer advances. Although both concomitant use rate in particular is not limited, 0.1-10 mol of radical initiators are suitable to 1 mol of radical capping agents.

[0044] As a radical generator, although various compounds can be used, the peroxide which may generate a radical is preferred under polymerization temperature conditions. Although limitation is not carried out, as this peroxide Benzoyl peroxide, Diacyl peroxide, such as lauroyl peroxide, JIKUMIRU peroxide, Dialkyl peroxide, such as di-t-butyl peroxide, diisopropyl peroxy dicarbonate, There are alkyls perester, such as peroxy carbonates, such as bis(4-t-butylcyclohexyl)peroxy dicarbonate, t-butyl peroxyoctoate, and t-butyl peroxybenzoate, etc. Especially benzoyl peroxide is preferred. Radical generators, such as a radical generating nature azo compound like azobisisobutyronitrile, can also be used instead of peroxide.

[0045] An alkoxy amine compound as shown in the following figure may be used as an initiator instead of using together a radical capping agent and a radical generator as reported by Macromolecules 1995, 28, and P.2993.

[0046]

[Formula 1]



If what has functional groups, such as a hydroxyl group that it is shown in the above figure, is used when using an alkoxy amine compound as an initiator, the polymer which has a functional group at the end will be obtained. If this is used for the method of this invention, the polymer which has a functional group at the end will be obtained.

[0047] Although polymerization conditions, such as the monomer and solvent which are used by the polymerization using radical scavengers, such as the above-mentioned nitroxide compound, and polymerization temperature, are not limited, they may be the same as that of what is used about the atom transfer radical polymerization explained below.

The more desirable atom-transfer-radical-polymerization method as atom transfer radical

polymerization, next living radical polymerization of this invention is explained.

[0048] The organic halogenated compound which has an organic halogenated compound, especially a reactant high carbon-halogen bond in this atom transfer radical polymerization. (For example, the carbonyl compound which has halogen in an alpha position and the compound which has halogen in a

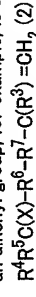
benzylic position), or a sulfonyl halide compound is used as an initiator. If it illustrates concretely, they will be  $C_6H_5-CH_2X$ ,  $C_6H_5-CH(H)X$ , and  $C_6H_5-CX(CH_3)_2$  (however, inside of upper chemical formula, and  $C_6H_5$  a phenyl group and X chlorine, bromine, or iodine).

$R^1-C(H)(X)-CO_2R^2$ ,  $R^1-C(CH_3)(X)-CO_2R^2$ ,  $R^1-C(H)(X)-C(O)R^2$ ,  $R^1-C(CH_3)(X)-C(O)R^2$  (as for the inside of a formula,  $R^1$  and  $R^2$ , a hydrogen atom or an alkyl group of the carbon numbers 1-20, an aryl group or an aralkyl group, and X are chlorine, bromine, or iodine).

$R^1-C_6H_4-SO_2X$  (as for inside of formula and  $R^1$ , a hydrogen atom or an alkyl group of the carbon numbers 1-20, an aryl group or an aralkyl group, and X are chlorine, bromine, or iodine) etc. is mentioned.

[0049] As an initiator of atom transfer radical polymerization, an organic halogenated compound or a sulfonyl halide compound which has functional groups other than a functional group which starts a polymerization can also be used. In such a case, a vinyl-base polymer which has a functional group in one main chain terminal, and has growth terminal structures of atom transfer radical polymerization in a main chain terminal of another side is manufactured. As such a functional group, an alkenyl group, crosslinkable silyl groups, hydroxyl, an epoxy group, an amino group, an amide group, etc. are mentioned.

[0050] What has the structure which it is not limited as an organic halogenated compound which has an alkenyl group, for example, is shown in a general formula (2) is illustrated.

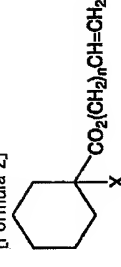


inside of formula, and  $R^3$  — hydrogen or a methyl group,  $R^4$  and  $R^5$  — hydrogen. Or a univalent alkyl group of the carbon numbers 1-20, an aryl group, an alkyl group or a thing mutually connected in the other end, and  $R^6$  — X in which C(O) O- (ester group), -C(O)- (keto group) or o-, m-, p-phenylene group, and  $R^7$  may include one or more ether bonds by a divalent organic group of direct coupling or the carbon numbers 1-20 is chlorine, bromine, or iodine.

As an example of substituent  $R^4$  and  $R^5$ , hydrogen, a methyl group, an ethyl group, n-propyl group, an isopropyl group, a butyl group, a pentyl group, a hexyl group, etc. are mentioned.  $R^4$  and  $R^5$  may be connected in the other end, and may form an annular skeleton.

[0051] As an example of an organic halogenated compound shown by a general formula (2) of having an alkenyl group,  $XCH_2C(O)CO[O(CH_2)_nCH=CH_2$  and  $H_3C(X)-C(O)O(CH_2)_nCH=CH_2$ , ( $H_3C$ ) $_2C(X)-C(O)O(CH_2)_nCH=CH_2$  and  $CH_3CH_2C(H)(X)-C(O)O(CH_2)_nCH=CH_2$ , [0052]

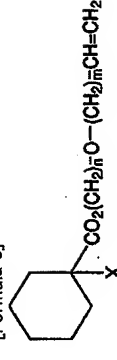
[Formula 2]



(In each of above-mentioned formulas, as for X, chlorine, bromine or iodine, and n are the integers of 0-20)

$XCH_2C(O)O(CH_2)_nCH=CH_2$ ,  $H_3CC(H)(X)C(O)O(CH_2)_nCH=CH_2$ , ( $H_3C$ ) $_2C(X)-C(O)O(CH_2)_nCH=CH_2$  and  $CH_3CH_2C(H)(X)-C(O)O(CH_2)_nCH=CH_2$ , [0053]

[Formula 3]



(As for chlorine, bromine or iodine, and n, in X, in each of above-mentioned formulas, the integer of 1-20 and m are the integers of 0-20)

o,m,p-XCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>, o,m,p-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>, O,m,p-CH<sub>3</sub>-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>

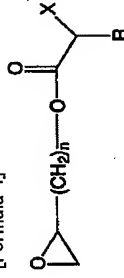




It is not limited especially as an organic halogenated compound with the above-mentioned epoxy group, or a sulfonyl halide compound, but the following is illustrated.

[0059]

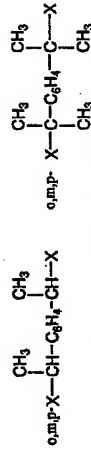
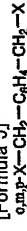
[Formula 4]



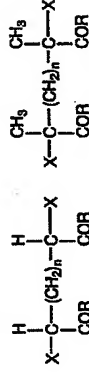
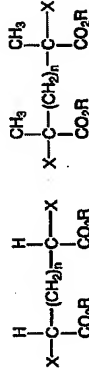
(As for chlorine, bromine or iodine, and R, in the inside of a formula, and X, a hydrogen atom or an alkyl group of the carbon numbers 1-20, an aryl group, an alkyl group, and n are the integers of 1-20)

In order to obtain a polymer which has two or more growth terminal structures in 1 intramolecular, it is preferred that an organic halogenated compound with the two or more starting points or a sulfonyl halide compound uses as an initiator. If it illustrates concretely, [0060]

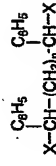
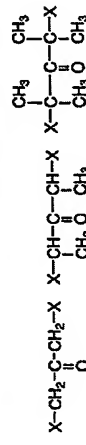
[Formula 5]



(式中、Xはフェニレン基、Xは塩素、臭素、またはヨウ素)



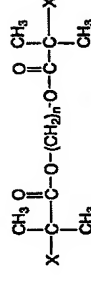
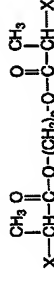
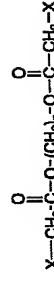
(式中、Rは炭数1~20のアシル基、アリール基、またはアラルキル基、nは0~20の整数、Xは塩素、臭素、またはヨウ素)



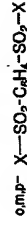
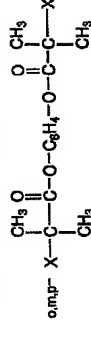
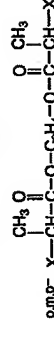
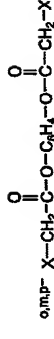
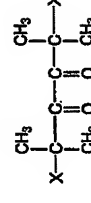
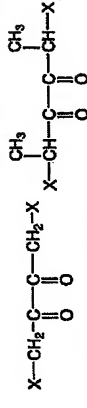
(式中、Xは塩素、臭素、またはヨウ素、nは0~20の整数)

[0061]

[Formula 6]



(式中、nは1~20の整数、Xは塩素、臭素、またはヨウ素)



(式中、Xは塩素、臭素、またはヨウ素)

\*\* is mentioned.

[0062]As a vinyl system monomer used in this polymerization, there are no restrictions in particular and all the already illustrated things can be used conveniently.

[0063]Although not limited especially as a transition metal complex used as a polymerization catalyst, it is a metal complex which uses the 7th fellows of the periodic table, eight fellows, nine fellows, ten fellows, or 11 group elements as a central metal preferably. As a desirable thing, a complex of zerovalent copper, univalent copper, a divalent ruthenium, divalent iron, or divalent nickel is mentioned. Especially, a copper complex is preferred. If a univalent copper compound is illustrated concretely, they will be a cuprous chloride, the first copper of bromination, a cuprous iodide, a cuprous cyanide, copper I oxide, the first copper of perchloric acid, etc. When using a copper compound, in order to improve catalytic activity 2,2'-bipyridyl and its derivative, Ligands, such as polyamine, such as a 1,10-phenanthroline and its derivative, tetramethylethylenediamine, pentamethyl diethylenetriamine, and hexamethyl tris(2-aminoethyl) amine, are added. A desirable ligand is a nitrogen-containing compound, a more desirable ligand is a chelate type nitrogen-containing compound, and still more desirable ligands are N, N', and N''-pentamethyl diethylenetriamine. A tris(phenyl) phosphine complex (RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>) of divalent ruthenium chloride is also preferred as a catalyst. When using a ruthenium compound as a catalyst, aluminum alkoxides are added as an activator. A screw triphenyl phosphine complex of divalent iron (FeCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>). A screw triphenyl phosphine complex (NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>) of divalent nickel and a screw tributyl phosphine complex (NiBr<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>) of divalent nickel are also preferred as a catalyst.

[0064]A polymerization can be performed in a non-solvent or various kinds of solvents. As a kind of

solvent, hydrocarbon system solvents, such as benzene and toluene, diethylether, Halogenated hydrocarbon system solvents, such as ether system solvents, such as a tetrahydrofuran, a methylene chloride, and chloroform, Ketone solvent, such as acetone, methyl ethyl ketone, and methyl isobutyl ketone, Methanol, ethanol, propanol, n-butyl alcohol, Alcoholic solvent, such as tert-butyl alcohol, acetonitrile, Carbonate system solvents, such as ester solvent, such as nitrile system solvents, such as propionitrile and benzonitrile, ethyl acetate, and butyl acetate, ethylene carbonate, and propylene carbonate, etc. are mentioned, and it can be independent, or two or more sorts can be mixed, and it can use.

[0065] Although limitation is not carried out, a polymerization can be performed in 0 \*\* - 200 \*\*, and it is 50-150 \*\* preferably.

[0066] What is called reverse atom transfer radical polymerization is also included in atom transfer radical polymerization of this invention. A high oxidation state when the usual atom-transfer-radical-polymerization catalyst generates a radical with reverse atom transfer radical polymerization. For example, it is the method of making general radical initiators, such as a peroxide, act and producing the equilibrium situation same as the result as atom transfer radical polymerization to Cu (II<sup>+</sup>) when Cu(I) is used as a catalyst (Macromolecules 1999, 32, 2872 references).

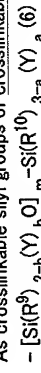
The number of crosslinkable silyl groups of a number vinyl-base polymer of <functional group> crosslinkable silyl groups, Although not limited in particular, it is preferred to have one or more pieces on the average from a viewpoint of the hardenability of a constituent and the physical properties of a hardened material, and it is 1.2 or more pieces [ 3.5 or less ] still more preferably 4.0 or less [ 1.1 or more ] more preferably.

As for at least one of a cross-linking functional group, since a molecular weight between the points constructing a bridge which has big influence on rubber elasticity can take greatly when especially rubber character is required of a hardened material which makes it come to harden a hardenability constituent of position this invention of crosslinkable silyl groups, it is preferred that it is in an end of a chain. It has all the cross-linking functional groups in molecular chain terminals more preferably.

[0067] A vinyl-base polymer which has the above-mentioned crosslinkable silyl groups in at least one molecular terminal, and a method of manufacturing an acrylic polymer especially (meta) are indicated by JP.H3-14068.B, JP.H4-55444.B, JP.H6-211922.A, etc. However, a polymer obtained since these methods are the free radical polymerizing methods for having used the above "chain transfer agent method", While it has crosslinkable silyl groups in molecular chain terminals at a comparatively high rate, it has the problem that a value of molecular weight distribution expressed with Mw/Mn is generally as large as two or more, and viscosity becomes high. Therefore, molecular weight distribution is narrow, and in order to obtain a vinyl-base polymer which has crosslinkable silyl groups in molecular chain terminals at a high rate, it is preferred [ it is a vinyl-base polymer with low viscosity, and ] to use the above "living-radical-polymerization method".

[0068] These functional groups are explained below.

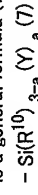
As crosslinkable silyl groups of crosslinkable-silyl-groups this invention, it is a general formula (6);



[Each of R<sup>9</sup> and R<sup>10</sup> among a formula An alkyl group of the carbon numbers 1-20, An aryl group of the carbon numbers 6-20, an aralkyl group of the carbon numbers 7-20, or (R<sup>9</sup>)<sub>3</sub>SiO - (R<sup>9</sup>) is a univalent hydrocarbon group of the carbon numbers 1-20, and) three R<sup>9</sup> being the same and differing — \*\*\*\* — when the Tori ORGANO siloxy group shown is shown and R<sup>9</sup> or two or more R<sup>10</sup> exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydrolytic basis and two or more Y exists, they may be the same and may differ. a shows 0, 1, 2, or 3, and b shows 0, 1, or 2. m is an integer of 0-19. However, it shall satisfy that it is a+mb>=1. A basis expressed with] is raised.

[0069] As a hydrolytic basis, a basis for which a hydrogen atom, an alkoxy group, an acyloxy group, a KETO-KISHI mate group, an amino group, an amide group, an aminoxy group, a sulfhydryl group, an alkenyloxy group, etc. are generally used, for example is raised. Among these, although an alkoxy group, an amide group, and an aminoxy group are preferred, a point of hydrolysis nature being mild and being easy to deal with it to especially an alkoxy group is preferred. Reactivity is high and a direction of what has a carbon number few in an alkoxy group is a methoxy group > ethoxy basis > propoxy group. — Reactivity becomes low and can choose it as order according to the purpose or a use.

[0070] A hydrolytic basis and a hydroxyl group can be combined with one silicon atom in the 1-3 ranges, and (a+sigma) has 1-5 preferred ranges. When a hydrolytic basis and a hydroxyl group join together in [ two or more ] crosslinkable silyl groups, they may be the same and may differ. Although a silicon atom which forms crosslinkable silyl groups is one or more pieces, in the case of a silicon atom connected by siloxane bond etc., it is preferred that they are 20 or less pieces. In particular, it is a general formula (7).



(R<sup>10</sup>, Y, and a are the same as the above among a formula.) — since crosslinkable silyl groups expressed is easy to receive, it is preferred.

[0071] Although limitation in particular is not carried out, when hardenability is taken into consideration, two or more pieces of a are preferred.

[0072] Although a polymer which has a hydrolytic silicon group which has two hydrolytic bases per silicon atom combine is used in many cases, a vinyl-base polymer which has such crosslinkable silyl groups, To take [ when using it at a use etc. and low temperature of adhesives and you need a very quick cure rate especially, the cure rate is not enough, and ] out pliability after hardening. Crosslinking density needed to be reduced, therefore since crosslinking density was not enough, there might be stickiness (surface tackiness). It is preferred that a is three things (for example, trimethoxy functional group) in that case.

[0073] Although three things (for example, trimethoxy functional group) have [ a ] hardenability quicker than two things (for example, dimethoxy functional group), about storage stability or dynamics physical properties (elongation etc.), a direction of two things may be excellent. In order to take hardenability and properties balance, two things (for example, dimethoxy functional group) and three things (for example, trimethoxy functional group) may be used together.

[0074] For example, since the reactivity of Y becomes high so that a has, when the same [ much Y ], by choosing various Y and a, it is possible to control hardenability, the mechanical physical property of a hardened material, etc. and it can choose according to the purpose or a use.

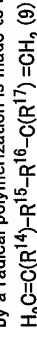
Although a method of introducing crosslinkable silyl groups to a vinyl-base polymer of this invention is explained below to a method of introducing crosslinkable silyl groups, it is not limited to this.

[0075] First, how to introduce crosslinkable silyl groups, an alkenyl group, and a hydroxyl group by end functional group conversion is described. Since these functional groups can serve as a precursor mutually, an order which goes back from crosslinkable silyl groups describes.

[0076] As a synthesizing method of a vinyl-base polymer which it has at least one piece, crosslinkable silyl groups, (A) A hydrosilane compound which has crosslinkable silyl groups in a vinyl-base polymer which has at least one alkenyl group. Like a compound which has crosslinkable silyl groups and an isocyanate group in a monad to a vinyl-base polymer which has at least one method (B) hydroxyl group made to add under hydrosilylation catalyst existence. When compounding a vinyl-base polymer by a method (C) radical polymerization to which a compound which has a basis which can react to a hydroxyl group is made to react, When compounding a vinyl-base polymer by a method (D) radical polymerization to which a compound it has a compound, and an alkenyl group and crosslinkable silyl groups of polymerization nature in one molecule is made to react, Method; etc. to which a compound which has stable carbanion with crosslinkable silyl groups in one molecule in a vinyl-base polymer which has at least one high carbon-halogen bond of method (E) reactivity which uses a chain transfer agent which has crosslinkable silyl groups is made to react are mentioned.

[0077] A vinyl-base polymer which has at least one alkenyl group used by a method of (A) is obtained by various methods. Although a synthesizing method is illustrated below, it is not necessarily limited to these.

[0078] (A-a) A method to which a compound it has a compound and an alkenyl group of polymerization nature and a low alkenyl group of polymerization nature in a monad which is mentioned, for example to the following general formula (9) when compounding a vinyl-base polymer by a radical polymerization is made to react as the 2nd monomer.



(R<sup>14</sup> shows hydrogen or a methyl group among a formula, R<sup>15</sup> shows -C(O) O- or o-, m-, and p-phenylene group, and R<sup>16</sup> may show a divalent organic group of direct coupling or the carbon

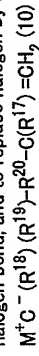
numbers 1-20, and may include one or more ether bonds.) R<sup>17</sup> shows hydrogen or an alkyl group of the carbon numbers 1-20, an aryl group of the carbon numbers 6-20, or an aralkyl group of the carbon numbers 7-20.

Although there is no restriction at a stage to which a compound it has a compound and an alkenyl group of polymerization nature and a low alkenyl group of polymerization nature in a monad is made to react, it is especially living radical polymerization. When it expects rubber character, it is preferred to make it react as the 2nd monomer after a telophase of a polymerization reaction or ending reaction of a predetermined monomer.

[0079](A-b) When compounding a vinyl-base polymer by living radical polymerization, A method to which a compound which has at least two low alkenyl groups of polymerization nature, such as 1,5-hexadiene, 1,7-octadiene, and 1,9-decadiene, for example is made to react after a telophase of a polymerization reaction, or ending reaction of a predetermined monomer.

[0080](A-c) How to make various kinds of organic metallic compounds which have an alkenyl group like organic tin, such as allyl tributyl tin and allyl trioctyl tin, for example react to a vinyl-base polymer which has at least one reactant high carbon-halogen bond, and to replace halogen by it.

[0081](A-d) How to make stabilization carbanion which has an alkenyl group which is mentioned to a general formula (10) react to a vinyl-base polymer which has at least one reactant high carbon-halogen bond, and to replace halogen by it.

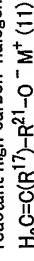


inside of formula, and R<sup>17</sup> — the above — the same — both R<sup>18</sup> and R<sup>19</sup> are electron withdrawing groups which stabilize carbanion C<sup>-</sup>, or, in one side, another side shows hydrogen, an alkyl group of the carbon numbers 1-10, or a phenyl group by said electron withdrawing group. R<sup>20</sup> may show a divalent organic group of direct coupling or the carbon numbers 1-10, and may include one or more ether bonds. M<sup>+</sup> shows alkali metal ion or the 4th class ammonium ion.

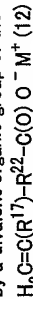
As an electron withdrawing group of R<sup>18</sup> and R<sup>19</sup>, especially a thing that has the structure of -CO<sub>2</sub>R, -C(O)R, and -ON is preferred.

[0082](A-e) To a vinyl-base polymer which has at least one reactant high carbon-halogen bond. For example, make a metal simple substance or an organic metallic compound like zinc act, and a eno rate anion is prepared. How to make after an appropriate time react to an electrophilicity compound which has alkenyl groups, such as an alkenyl group content compound which has a leaving group like halogen or an acetyl group, a carbonyl compound which has an alkenyl group, an isocyanate compound which has an alkenyl group, and acid halide which has an alkenyl group.

[0083](A-f) How to make a oxy anion or a carboxylate anion which has an alkenyl group as shown, for example in the general formula (11) or (12) react to a vinyl-base polymer which has at least one reactant high carbon-halogen bond, and to replace halogen by it.



(R<sup>17</sup> and M<sup>+</sup> are the same as the above among a formula.) R<sup>21</sup> may include one or more ether bonds by a divalent organic group of the carbon numbers 1-20.



(R<sup>17</sup> and M<sup>+</sup> are the same as the above among a formula.) It is mentioned that R<sup>22</sup> may include one or more ether bonds by a divalent organic group of direct coupling or the carbon numbers 1-20 etc.

[0084]A synthetic method of a vinyl-base polymer which has at least one above-mentioned reactant high carbon-halogen bond uses the above organic halogenated compounds etc. as an initiator, and although an atom-transfer-radical-polymerization method which makes a transition metal complex a catalyst is mentioned, it is not necessarily limited to these.

[0085]Although a vinyl-base polymer which has at least one alkenyl group is possible also for obtaining from a vinyl-base polymer which has at least one hydroxyl group and can use a method of illustrating below, it is not necessarily limited to these. How to make a base like sodium methoxide act on a hydroxyl group of a vinyl-base polymer which has at least one hydroxyl group, and make it react to an alkenyl group content halogenide like an allyl chloride.

[0086](A-h) A method to which alkenyl group content isocyanate compounds, such as an allylisocyanate, are made to react.

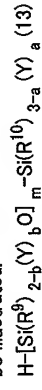
[0087](A-i) A method (meta) to which alkenyl group content acid halide like acrylic acidchloride is made to react under base existence, such as pyridine.

[0088](A-j) Method; etc. which make alkenyl group content carboxylic acid, such as acrylic acid, react under existence of an acid catalyst are mentioned.

[0089]When halogen does not participate in a method of introducing an alkenyl group like this invention (A-a) (A-b) directly, it is preferred to compound a vinyl-base polymer using a living-radical polymerization method. A method of a point that control is easier to (A-b) is still more preferred.

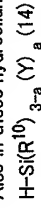
[0090]When introducing an alkenyl group by changing halogen of a vinyl-base polymer which has at least one reactant high carbon-halogen bond. An organic halogenated compound which has at least one reactant high carbon-halogen bond. Or it is preferred to use a vinyl-base polymer which is obtained by using a sulfonyl halide compound as an initiator and carrying out the radical polymerization of the vinyl system monomer by making a transition metal complex into a catalyst (atom-transfer-radical-polymerization method) and which has at least one reactant high carbon-halogen bond at the end. A method of a point that control is easier to (A-f) is still more preferred.

[0091]Although there is no restriction in particular as a hydrosilane compound which has crosslinkable silyl groups, if a typical thing is shown, a compound shown by a general formula (13) will be illustrated.



[Each of R<sup>9</sup> and R<sup>10</sup> among a formula An alkyl group of the carbon numbers 1-20, An aryl group of the carbon numbers 6-20, an aralkyl group of the carbon numbers 7-20, or (R<sup>9</sup>)<sub>3</sub>SiO - (R<sup>10</sup>)<sub>3</sub> is a univalent hydrocarbon group of the carbon numbers 1-20, and) three R<sup>i</sup> being the same and differing — \*\*\*\* — when the Tori ORGANO siloxy group shown is shown and R<sup>9</sup> or two or more R<sup>10</sup> exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydrolytic basis and two or more Y exists, they may be the same and may differ. a shows 0, 1, 2, or 3, and b shows 0, 1, or 2. m is an integer of 0-19. However, it shall satisfy that it is a+mb>=1.]

Also in these hydrosilane compound, it is especially a general formula (14).

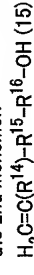


a compound which has a cross-linking group shown by (the inside of a formula, R<sup>10</sup>, Y, and a are the same as the above) — acquisition — it is desirable from an easy point.

[0092]When making a hydrosilane compound which has the above-mentioned crosslinkable silyl groups add to an alkenyl group, a transition metal catalyst is usually used. A thing which, for example, made carriers, such as a platinum simple substance, alumina, silica, and carbon black, distribute a platinum solid as a transition metal catalyst, A complex with chloroplatinic acid, chloroplatinic acid, alcohol, aldehyde, ketone, etc., a platinum-olefin complex, and a platinum (0)-divinyl tetramethyl disiloxane complex are mentioned. As an example of catalysts other than a platinum compound, RhCl (PPh<sub>3</sub>)<sub>3</sub>, RhCl<sub>3</sub>, RuCl<sub>3</sub>, IrCl<sub>3</sub>, FeCl<sub>3</sub>, PdCl<sub>2</sub>-H<sub>2</sub>O, NiCl<sub>2</sub>, TiCl<sub>4</sub>, etc. are mentioned.

[0093](B) And a manufacturing method of a vinyl-base polymer which has at least one hydroxyl group used by a method of (A-g) - (A-j) is not limited to these methods, although following methods are illustrated.

[0094](B-a) A method to which a compound it has a compound, and an alkenyl group and a hydroxyl group of polymerization nature in a monad which is mentioned, for example to the following general formula (15) when compounding a vinyl-base polymer by a radical polymerization is made to react as the 2nd monomer.



(The inside of a formula, R<sup>14</sup>, R<sup>15</sup>, and R<sup>16</sup> are the same as the above)

Although there is no restriction at a stage to which a compound it has a compound, and an alkenyl group and a hydroxyl group of polymerization nature in a monad is made to react, it is especially living radical polymerization, and when it expects rubber character, it is preferred to make it react as the 2nd monomer after a telophase of a polymerization reaction or ending reaction of a predetermined monomer.

[0095](B-b) A method to which 10-UNDESE Norian, 5-hexenol, and alkenyl alcohol like allyl alcohol are made to react after a telophase of a polymerization reaction, or ending reaction of a

predetermined monomer for example when compounding a vinyl-base polymer by living radical polymerization.

[0096](B-c) For example, a method of carrying out the radical polymerization of the vinyl system monomer, using so much a hydroxyl group content chain transfer agent like hydroxyl group content polysulfide shown in JP,5-262808.A.

[0097](B-d) For example, a method of carrying out the radical polymerization of the vinyl system monomer using hydrogen peroxide or a hydroxyl group content initiator as shown in JP,6-239912.A and JP,8-283310.A.

[0098](B-e) For example, a method of carrying out the radical polymerization of the vinyl system monomer, using alcohols as shown in JP,6-116312.A, superfluously.

[0099](B-f) For example, a method of introducing a hydroxyl group into an end by making halogen of a vinyl-base polymer which has a reactant high carbon-halogen bond in at least one piece react to hydrolysis or hydroxyl group-containing compound by a method as shown in JP,4-132706.A etc.

[0100](B-g) How to make stabilization carbanion which has a hydroxyl group which is mentioned to a general formula (16) react to a vinyl-base polymer which has at least one reactant high carbon-halogen bond, and to replace halogen by it.

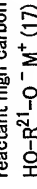


(It is the same as the inside of a formula, and  $R^{18}$ ,  $R^{19}$ ,  $R^{20}$  and \*\*\*\*\*)

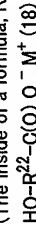
As an electron withdrawing group of  $R^{18}$  and  $R^{19}$ , especially a thing that has the structure of  $-CO_2R$ ,  $-C(O)R$ , and  $-CN$  is preferred.

[0101](B-h) How to, make a metal simple substance or an organic metallic compound like zinc act on a vinyl-base polymer which has at least one reactant high carbon-halogen bond for example, to prepare a eno rate anion, and to make aldehyde or ketone react to after an appropriate time.

[0102](B-i) How to make a oxy anion or a carboxylate anion which has a hydroxyl group as shown, for example in the general formula (17) or (18) react to a vinyl-base polymer which has at least one reactant high carbon-halogen bond, and to replace halogen by it.



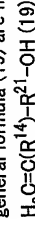
(The inside of a formula,  $R^{21}$ , and  $M^+$  are the same as the above)



(The inside of a formula,  $R^{22}$ , and  $M^+$  are the same as the above)

(B-j) A method to which a compound which has a low alkenyl group and a hydroxyl group of a polymerization nature in a monad is made to react as the 2nd monomer after a telophase of a polymerization reaction, or ending reaction of a predetermined monomer when compounding a vinyl-base polymer by living radical polymerization.

[0103]Although not limited especially as such a compound, a compound etc. which are shown in a general formula (19) are mentioned.



( $R^{14}$  and  $R^{21}$  are the same as that of what was mentioned above among a formula.)

Although not limited especially as a compound shown in the above-mentioned general formula (19), since it says that acquisition is easy, 10-UNDESE Norian, 5-hexenol, and alkenyl alcohol like allyl alcohol are preferred. \*\* is mentioned.

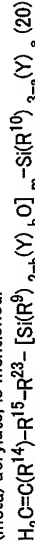
[0104]When halogen does not participate in a method of introducing a hydroxyl group like (B-a) - (B-e), and (B-j) in this invention directly, it is preferred to compound a vinyl-base polymer using a living-radical-polymerization method. A method of of a point that control is easier to (B-b) is still more preferred.

[0105]When introducing a hydroxyl group by changing halogen of a vinyl-base polymer which has at least one reactant high carbon-halogen bond, . Obtain by using an organic halogenated compound or a sulfonyl halide compound as an initiator, and carrying out the radical polymerization of the vinyl system monomer by making a transition metal complex into a catalyst (atom-transfer-radical-polymerization method). It is preferred to use for an end a vinyl-base polymer which has at least one reactant high carbon-halogen bond. A method of of a point that control is easier to (B-i) is still more preferred.

[0106]As a compound which has in a monad a basis which can react to crosslinkable silyl groups and

a hydroxyl group like an isocyanate group, For example, gamma-isocyanate propyltrimethoxysilane, gamma-isocyanate propylmethyl dimethoxysilane, gamma-isocyanate propyl triethoxysilane, etc. are mentioned, and a catalyst of a urethane-ized reaction generally known as occasion demands can be used.

[0107]As a compound it has a compound, and an alkenyl group and crosslinkable silyl groups of polymerization nature in a monad used by a method of (G). For example, what is shown with following general formulas (20), such as trimethoxysilylpropyl (meta) acrylate and methyl dimethoxy silyl propyl (meta) acrylate, is mentioned.

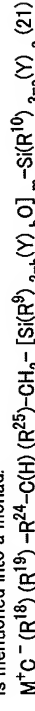


( $R^9$ ,  $R^{10}$ ,  $R^{14}$ ,  $R^{15}$ ,  $Y$ ,  $a$ ,  $b$ , and  $m$  are the same as the above among a formula.)  $R^{23}$  may include one or more ether bonds by a divalent organic group of direct coupling or the carbon numbers 1-20.

Especially although there is no restriction in particular at a stage to which a compound it has a compound, and an alkenyl group and crosslinkable silyl groups of polymerization nature in a monad is made to react, it is living radical polymerization. When it expects rubber character, it is preferred to make it react as the 2nd monomer after a telophase of a polymerization reaction or ending reaction of a predetermined monomer.

[0108]Hydrosilane etc. which have mercaptan which has crosslinkable silyl groups and crosslinkable silyl groups which are used by a chain transfer agent method of (D), and which are shown in JP,3-14068.B and JP,4-55444.B as a chain transfer agent which has crosslinkable silyl groups are mentioned.

[0109]A synthetic method of a vinyl-base polymer which has at least one above-mentioned reactant high carbon-halogen bond used by a method of (E) uses the above organic halogenated compounds etc. as an initiator, and although an atom-transfer-radical-polymerization method which makes a transition metal complex a catalyst is mentioned, it is not necessarily limited to these. What is shown by a general formula (21) as a compound having crosslinkable silyl groups and stabilization carbanion is mentioned into a monad.



(It is the same as  $R^9$ ,  $R^{10}$ ,  $R^{18}$ ,  $R^{19}$ ,  $Y$ ,  $a$ ,  $b$ ,  $m$ , and \*\*\*\*\* among a formula.)  $R^{25}$  in which  $R^{24}$  may include one or more ether bonds by a divalent organic group of direct coupling or the carbon numbers 1-10 shows hydrogen or an alkyl group of the carbon numbers 1-10, an aryl group of the carbon numbers 6-10, or an aralkyl group of the carbon numbers 7-10.

As an electron withdrawing group of  $R^{18}$  and  $R^{19}$ , especially a thing that has the structure of  $-CO_2R$ ,  $-C(O)R$ , and  $-CN$  is preferred.

In a hardenability constituent of <polyether system polymer (II) which averages and has 1.2 or less crosslinkable silyl groups> X main chain> this invention. As main chain structure of polyether system polymer (II) which averages and has 1.2 or less crosslinkable silyl groups, polyoxyalkylene expressed with general formula-(R-O)-n- (the inside of a formula and R are the divalent alkylene groups of the carbon numbers 1-4) is preferred. If it illustrates concretely, a polyoxyethylene, polyoxypropylene, polyoxy butylene, polyoxy hexylene, polyoxy tetramethylen, these copolymer, etc. will be mentioned. inside --- acquisition --- an easy point to polyoxypropylene is preferred. This polyoxypropylene may be straight chain shape, may be a letter of branching, or may be these mixtures. Especially desirable things are polyoxypropylene diol, polyoxypropylene triol, and those mixtures also in it. Although other monomeric units may be included, it is preferred that 80 % of the weight or more of monomeric units expressed to the above-mentioned formula exist preferably 50% of the weight or more in a polymer.

[0110]A urethane bond or urea combination may be included in a main chain, and it is not necessary to contain.

[0111]Molecular structure of polyether system polymer (II) of this invention is different with the characteristic made into usage or the purpose, and a method given in JP,63-112642.A etc. can be used for it. It is preferred that it is an oxyalkylene polymer which is the amount of Polymer Division, and molecular weight distribution (Mw/Mn) is small and has a functional group from a viewpoint of reconciling hypoviscosity-izing (workability) of a hardenability constituent, and a low modulus of a hardened material which stiffened it and a raise in elongation. As for a number average molecular weight, 12,000 or less [ 300 or more ] are preferred, and, specifically, 8,000 or less [ 300 or more ]

are more preferred. As for Mw/Mn, 1.6 or less are preferred, and 1.5 or less are still more preferred. Although it is difficult to obtain such polyoxalkylene by the usual polymerization method (anionic polymerization method using a caustic alkali), or the elongation reaction method of this polymer. For example, a caesium metal catalyst, JP 61-197631A, JP 61-215622A, The porphyrin / aluminum complex compound catalyst illustrated by JP 61-215623A, JP 61-218632A, etc., it can be obtained by a method using a composite metal cyanidation complex compound catalyst illustrated by JP 46-27250B, JP 59-15336B, etc. and a catalyst which consists of a polyphosphazene salt illustrated by JP 10-273512A, etc. Practically, a method of using a composite metal cyanidation complex compound catalyst is preferred.

In polyether system polymer (II) which <crosslinkable-silyl-groups> this invention averages and has 1.2 or less crosslinkable silyl groups, a bond part between crosslinkable silyl groups and a polyether part. Since it has hydrolysis resistance, it is preferred that it is an alkylene group like trimethylene and tetramethylene so that at least three carbon atoms may exist between a silicon atom of a silyl group, and an ether acid matter atom of a polyether part.

The number of crosslinkable silyl groups and the number of crosslinkable silyl groups of polyether system polymer (II) in position this invention are averaged, and are 1.2 or less pieces, on the other hand, if there are too few silyl groups, in order not to reveal an effect of this invention, it is preferred that they are at least 0.1 or more pieces, it is more preferred that they are 0.3 or more pieces, and it is still more preferred that they are 0.5 or more pieces. It is preferred that it is in an end of a chain. Although what it has only at the one end in a main chain, and does not have in other ends is preferred as for crosslinkable silyl groups of this polyether system polymer (II), it averages, and it will not be limited especially if it is 1.2 or less pieces.

As for polyether system polymer (II) which the introductory Homoto invention of crosslinkable silyl groups averages, and has 1.2 or less crosslinkable silyl groups, it is preferred to obtain by introducing crosslinkable silyl groups into a polyether system polymer which has a functional group.

[0112]What is necessary is just to perform introduction of crosslinkable silyl groups by a publicly known method. That is, for example, the following methods are mentioned. For example, in the case of an oxalkylene polymer in which it is obtained considering a polyphosphazene salt and active hydrogen as a catalyst by JP 3-72527A in the case of an oxalkylene polymer obtained using a composite metal cyanidation complex compound catalyst, it is indicated to JP 11-60723A.

[0113](1) Make an oxalkylene polymer which has functional groups, such as a hydroxyl group, and an organic compound which has an active group and an unsaturation group in which reactivity is shown to this functional group react to an end, or obtain an unsaturation group content oxalkylene polymer by copolymerization with an unsaturation group content epoxy compound. Subsequently, hydrosilane which has crosslinkable silyl groups is made to act on an acquired resultant, and it hydrosilylates. [0114](2) and (1) — a compound which has a sulfinyl group and crosslinkable silyl groups is made to react to an unsaturation group content oxalkylene polymer produced by making it be the same as that of law

[0115](3) Make a compound which has a functional group (henceforth Y' functional group) and crosslinkable silyl groups which show reactivity to an oxalkylene polymer which has functional groups (henceforth Y functional group), such as a hydroxyl group, an epoxy group, and an isocyanate group, to this Y functional group react to an end.

[0116]As a silicon compound which has this Y' functional group, gamma-(2-aminoethyl) aminopropyl trimethoxysilane, gamma-(2-aminoethyl) aminopropyl methyl dimethoxysilane, Amino group content Siliang, such as gamma-aminopropyl triethoxysilane; gamma-mercaptopropyltrimethoxysilane, Sulfinyl group content Siliang, such as gamma-mercaptopropylmethyl dimethoxysilane; Gamma-glycidioxypropyltrimethoxysilane, Epoxysilane, such as beta-(3, 4-epoxyoxyclohexyl) ethyltrimethoxysilane; Vinyltriethoxysilane, gamma-methacryloyl oxypropyl trimethoxysilane, vinyl type unsaturation group content Siliang [ such as gamma-acryloyloxypropylmethyl dimethoxysilane, ]; — chlorine atom content Siliang [ such as gamma-chloropropyltrimethoxysilane, ]; — gamma-isocyanatepropyl triethoxysilane. Isocyanate content Siliang, such as gamma-isocyanate propylmethyl dimethoxysilane and gamma-isocyanate propyltrimethoxysilane; Methyl dimethoxysilane, trimethoxysilane, methyldiethoxysilane, Although hydro-Siliang, such as triethoxysilane, is illustrated concretely and they get, it is not limited to these.

[0117]By making a compound which has the crosslinkable silyl groups of the functional group and

equivalent, or a smaller quantity using a polyether system polymer which merely has a functional group of a piece react to intramolecular, when introducing crosslinkable silyl groups. How to obtain a polyether system polymer which averages crosslinkable silyl groups and it has 1.2 or less pieces. There is a method of obtaining a polyether system polymer which averages crosslinkable silyl groups as a result, and it has 1.2 or less pieces by making a compound which has still less crosslinkable silyl groups rather than the functional group react using a polyether system polymer which averages and has a functional group more than a piece in intramolecular.

The amount of polyether system polymer (II) used which averages and has 1.2 or less crosslinkable silyl groups average as amount of polyether system polymer (II) used which carries out and has 1.2 or less crosslinkable silyl groups. As for polyether system polymer (II) which has 1.2 or less crosslinkable silyl groups on the average to vinyl-base polymer (I) 100 weight section, 200 or less pairs more than per weight section are preferred. Its 100 or less weight section three or more-weight section is more preferred, and its 80 or less weight section five or more-weight section is still more preferred.

In a hardenability constituent of <<polyether system polymer (II)> which has at least 1.2 or more cross-linking functional groups>> main chain> this invention, As polyether system polymer (III) which has at least 1.2 or more cross-linking functional groups, Polyoxalkylene expressed with general formula  $-(R-O)-n-$  (the inside of a formula and R are the divalent alkylene groups of the carbon numbers 1-4) is preferred as well as main chain structure of polyether system polymer (II) which averages and has 1.2 or less crosslinkable silyl groups. It can be illustrated that polyether system polymer (II) which specifically averages and has 1.2 or less crosslinkable silyl groups indicated. Although other monomeric units may be included, it is preferred that 80 % of the weight or more of monomeric units expressed to the above-mentioned formula exist preferably 50% of the weight or more in a polymer.

[0118]A urethane bond or urea combination may be included in a main chain, and it is not necessary to contain.

[0119]Molecular structure of polyether system polymer (III) of this invention is different with the characteristic made into usage or the purpose, and a method given in JP 63-112642A etc. can be used for it. It is preferred that it is an oxalkylene polymer with small molecular weight distribution (Mw/Mn) which is the amount of Polymer Division from a viewpoint of reconciling hypoviscosity-izing (workability) of a hardenability constituent, and a low modulus of a hardened material which stiffened it and a raise in elongation. As for a number average molecular weight, 50,000 or less [ 5,000 or more ] are preferred, and, specifically, 20,000 or less [ 8,000 or more ] are more preferred. As for Mw/Mn, 1.6 or less are preferred, and 1.5 or less are still more preferred. A manufacturing method of such polyoxalkylene is the same as polyether system polymer (II) which \*\*\* averages and has 1.2 or less crosslinkable silyl groups indicated.

In polyether system polymer (III) which it has, at least 1.2 or more cross-linking functional groups of <crosslinkable-silyl-groups> this invention a bond part between crosslinkable silyl groups and a polyether part. Since it has hydrolysis resistance, it is preferred that it is an alkylene group like trimethylene and tetramethylene so that at least three carbon atoms may exist between a silicon atom of a silyl group, and an ether acid matter atom of a polyether part.

As for the number of crosslinkable silyl groups, and the number of crosslinkable silyl groups of polyether system polymer (III) in position this invention, it is preferred to have from viewpoints of the hardenability of a constituent, etc. more mostly than at least 1.2 pieces, it is 1.5-2.5 or less pieces that it is [ 1.2 or more piece ] 4.0 or less more desirable still more preferably. As for crosslinkable silyl groups which is this polyether system polymer (III), it is preferred that it is in an end of a chain from a viewpoint of the rubber elasticity of a hardened material, and it is that both ends of a polymer have a functional group more preferably.

As for polyether system polymer (III) which has at least 1.2 or more cross-linking functional groups of the introductory Homoto invention of crosslinkable silyl groups, it is preferred to obtain by introducing the crosslinkable silyl groups into a polyether system polymer which has a functional group.

[0120]What is necessary is just to perform introduction of crosslinkable silyl groups by a publicly known method. A method indicated by polyether system polymer (II) which specifically averages and has 1.2 or less crosslinkable silyl groups is mentioned.

<the amount of polyether system polymer (III) used which has at least 1.2 or more cross-linking



functional groups> — as amount of polyether system polymer (III) used which has at least 1.2 or more cross-linking functional groups. The mixture ratio of vinyl-base polymer (I) and polyether system polymer (III) has the preferred range of  $100 / 1 - 1/100$  at a weight ratio, it is more preferred that it is in the range of  $100 / 5 - 5/100$ , and it is still more preferred that it is in the range of  $100 / 10 - 10/100$ . When there is too little quantity of vinyl-base polymer (I), weatherability and heat resistance may fall.

In a hardenability constituent of < hardenability constituent >> this invention, there are some for which a curing catalyst and a hardening agent are needed. Various kinds of combination drugs may be added according to the target physical properties.

By forming a siloxane bond under existence of various publicly known condensation catalysts or nonexistence conventionally, a polymer which has < curing catalyst and hardening agent > crosslinkable silyl groups constructs a bridge, and is hardened. As description of a hardened material, it can create broadly from a rubber-like thing to a resin-like thing according to a molecular weight and a principal chain skeleton of a polymer.

[0121]As such a condensation catalyst, for example Dibutyltin dilaurate, dibutyltin diacetate, A dibutyl tin diethylhexanoate, dibutyl tin JIOKUTETO, dibutyl tin dimethylmalate, Dibutyl tin diethyl malate, dibutyl tin dibutyl maleate, dibutyl tin diisooctyl malate, Dibutyl tin ditridecyl malate, dibutyl tin dibenzyl malate, Dibutyltin maleate, dioctyl tin diacetate, dioctyl tin distearate, Tetravalent tin compounds, such as dioctyl tin dilaurate, dioctyl tin diethyl malate, and dioctyl tin diisooctyl malate; Tin octylate, Monoalkyl tin, such as monobutyl tin compounds, such as divalent tin compound; monobutyl tin tris octoate, such as naphthenic acid tin and tin stearate, and monobutyl tin TORISO propoxide, and a monoocetyl tin compound; Tetrabutyl titanate, Titanate, such as tetrapropyl titanate; Aluminum tris acetylacetonate, Organoaluminum compounds, such as aluminumtrisethylacetoacetate and diisopropoxy aluminum ethylacetoacetate; Carboxylic acid vanadium, a carboxylic acid zirconium, carboxylic acid titanium, Carboxylic acid lead, carboxylic acid vanadium, a carboxylic acid iron, carboxylic acid calcium, Carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, carboxylic acid cerium, carboxylic acid (2-ethylhexanoic acid), such as carboxylic acid nickel, carboxylic acid cobalt, carboxylic acid zinc, and carboxylic acid aluminum Metal salt, such as neo decanoic acid, BASA tic acid, oleic acid, and naphthenic acid, Or a reactant and mixtures with an amine compound, such as these and the below-mentioned lauryl amine; Zirconium tetra acetylacetonate, Chelate compound, such as titanium tetra acetylacetonate; Methylamine, Ethylamine, propylamine, isopropylamine, a butylamine, Amyl amine, hexylamine, octylamine, 2-ethylhexylamine, Nonyl amine, decyl amine, lauryl amine, pentadecyl amine, Aliphatic series primary amines, such as Sept. Iles amine, stearylamine, and cyclohexylamine; Dimethylamine, Diethylamine, dipropyl amine, diisopropylamine, dibutyl amine, diamylamine, dioctyl amine, di(2-ethylhexyl) amine, didecyl amine, dilauryl amine, JISECHIRU amine, distearyl amine, methylstearylamine, ethylstearylamine, Aliphatic series secondary amines, such as butylstearylamine; Triamylamine, Aliphatic series tertiary amines, such as trihexyl amine and trioctylamine; Triaryl amine, Aliphatic series unsaturation amines, such as oleylamine; as aromatic amine [ such as lauryl aniline stearylamine, and a triphenylamine, ] and other amines, Monoethanolamine, diethanolamine, triethanolamine, Diethylenetriamine, triethylenetetramine, oleylamine, Cyclohexylamine, benzylamine, diethylamino propylamine, Xylene diamine, ethylenediamine, hexamethylenediamine, Triethylenediamine, guanidine, diphenylguanidine, 2,4,6-tris(dimethyl aminomethyl) phenol, Amine compounds, such as morpholine, N-methylmorpholine, 2-ethyl-4-methylimidazole, 1, and 8-diazabicyclo (5, 4, 0) undecene 7 (DBU). Or salt [ with carboxylic acid of these amine compounds, etc. ]. A reactant of lauryl amine and tin octylate, or a reactant of an amine compound and an organic tin compound like a mixture and mixture; — low-molecular-weight-polyamide resin; obtained from superfluous polyamine and polybasic acid — resultant; gamma-aminopropyl trimethoxysilane of superfluous polyamine and an epoxy compound, gamma-aminopropyl triethoxysilane, gamma-aminopropyl trimethoxysilane, N-(beta-aminoethyl) aminopropyl trimethoxysilane, N-(beta-aminoethyl) aminopropyl methyl dimethoxysilane, N-(beta-aminoethyl) aminopropyl triethoxysilane, N-(beta-aminoethyl) aminopropyl methyldiethoxysilane, N-(beta-aminoethyl) aminopropyl triisopropyl silane, aminoethyl) aminopropyl methyldiethoxysilane, N-(beta-aminoethyl) aminopropyl triisopropyl silane, gamma-ureido propyltrimethoxysilane, N-phenyl-gamma-aminopropyl trimethoxysilane, N-benzyl-gamma-aminopropyl trimethoxysilane, N-vinylbenzyl gamma-aminopropyl triethoxysilane etc. can be

mentioned. Amino modifying silyl polymer which is the derivative which denaturalized these, Publicly known silanol condensation catalysts, such as silanol condensation catalysts, such as silane coupling agent; which has amino groups, such as silanizing amino polymer, an unsaturation aminosilane complex, a phenylamino long chain alkyl silane, and amino silanizing silicone, an acid catalyst of further others, and a basic catalyst, etc. can be illustrated.

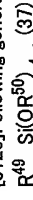
[0122]These catalysts may be used alone and may be used together two or more sorts. As for loadings of this condensation catalyst, about 0.1–20 copies are preferred to 100 copies (it is [ a weight section and the following ] the same) of vinyl-base polymers which have at least one crosslinkable silyl groups, and its 1–10 copies are still more preferred. If loadings of a silanol condensation catalyst are less than this range, a cure rate may become slow and a hardening reaction will become fully difficult to advance. On the other hand, pot life becomes short too much and is not preferred from a point of workability except that a good hardened material will become generation of heat and foaming local at the time of hardening arise, and is hard to be obtained, if loadings of a silanol condensation catalyst exceed this range. Although limitation in particular is not carried out, in order to control hardenability, it is preferred to use a tin system curing catalyst.

[0123]In a hardenability constituent of this invention, in order to improve the activity of a condensation catalyst more, it is also possible to use a silane coupling agent which has the above-mentioned amino group as a co-catalyst like an amine compound. Although this amino group content silane coupling agent is a compound which has a basis (henceforth a hydrolytic silicon group) and an amino group containing a silicon atom which a hydrolytic basis combined and a basis already illustrated as this hydrolytic basis can be mentioned. A methoxy group, an ethoxy basis, etc. are preferred from a point of a hydrolysis rate. As for especially the two or more number of a hydrolytic basis, three or more pieces are preferred.

[0124]As for loadings of these amine compounds, about 0.01–50 weight sections are preferred to organic polymer 100 weight section of vinyl-base polymer (I), and also its 0.1 to 20 weight section is more preferred. A cure rate may become it slow that loadings of an amine compound are less than 0.01 weight sections, and a hardening reaction becomes fully difficult to advance. On the other hand, if loadings of an amine compound exceed 30 weight sections, pot life may become short too much and is not preferred from a point of workability.

[0125]These amine compounds may be used only by one kind, and may carry out two or more kind mixing use.

[0126]Following general formula (37)



( $R^{49}$  and  $R^{50}$  are substitution or unsubstituted hydrocarbon groups of the carbon numbers 1–20 independently among a formula, respectively,) a is 0, 1, 2, or 3. A silicon compound without neither an amino group shown nor a silanol group may be added as a co-catalyst.

[0127]Although limitation is not carried out, as said silicon compound Phenyltrimethoxysilane, Phenylmethyldimethoxysilane, phenyldimethylmethoxysilane, Since the effect that what is an aryl group of the carbon numbers 6–20 accelerates a hardening reaction of a constituent is large,  $R^{49}$  in general formulas (37), such as diphenyldimethoxysilane, diphenyl diethoxysilane, and triphenylmethoxysilane, is preferred. Especially diphenyldimethoxysilane and diphenyl diethoxysilane are low cost, and since they are easy to receive, they are the most preferred.

[0128]As for loadings of this silicon compound, about 0.01–20 copies are preferred to 100 copies of vinyl-base polymers, and its 0.1–10 copies are still more preferred. If loadings of a silicon compound are less than this range, an effect of accelerating a hardening reaction may become small. On the other hand, when loadings of a silicon compound exceed this range, hardness and tensile strength of a hardened material may fall.

[0129]A kind and an addition of a curing catalyst and a hardening agent can be chosen with a kind of Y of a vinyl-base polymer expressed with the general formula (1) and (6) of this invention, or the number of a, and can control hardenability, a mechanical physical property, etc. of this invention according to the purpose or a use. When Y is an alkoxy group, a direction with few carbon numbers has high reactivity, and it is possible for a to make it harden enough in a small quantity, since more ones have high reactivity.

In a constituent of < adhesive grant agent > this invention, a silane coupling agent and adhesive grant

agents other than a silane coupling agent can be added. If an adhesion grant agent is added, when changing joint width etc. with external force, a danger that a sealing material will exfoliate from adherends, such as a siding board, can be reduced more. By a case, the necessity for use of a primer of using for adhesive improvement is lost, and simplification of construction is expected. As an example of a silane coupling agent, an amino group and a sulfinyl group, Can illustrate a silane coupling agent with functional groups, such as an epoxy group, a carboxyl group, a vinyl group, an isocyanate group, isocyanurate, and halogen, and as the example, gamma-isocyanate propyltrimethoxysilane, gamma-isocyanatopropyl triethoxysilane, Isocyanate group content Silang, gamma-aminopropyl trimethoxysilane, such as gamma-isocyanate propylmethyl diethoxysilane and gamma-isocyanate propylmethyl dimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-aminopropyl triisopropoxy silane, gamma-(2-aminoethyl) aminoethyl triethoxysilane, gamma-(2-aminoethyl) aminoethyl methyl dimethoxysilane, gamma-(2-aminoethyl) aminoethyl methyl dimethoxysilane, gamma-(2-aminoethyl) aminoethyl triethoxysilane, N-phenyl-gamma-aminopropyl trimethoxysilane, N-benzyl-gamma-aminopropyl trimethoxysilane, Amino group content Silang, such as N-vinylbenzyl gamma-aminopropyl triethoxysilane; gamma-mercaptopropyltrimethoxysilane, gamma-mercaptopropyl triethoxysilane, gamma-mercaptopropylmethyl dimethoxysilane, Sulfinyl group content Silang, such as gamma-mercaptopropylmethyl diethoxysilane; Gamma-glycidoxypolytrimethoxysilane, gamma-glycidoxypolytriethoxysilane, gamma-glycidoxypolypropyl dimethoxysilane, beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, Epoxy group content Silang, such as beta-(3,4-epoxycyclohexyl) ethyltriethoxysilane; beta-carboxyethyl triethoxysilane, beta-carboxyethyl phenylbis(2-methoxyethyl)Silang, Carboxysilanes, such as N-beta-(carboxymethyl) aminoethyl gamma-aminopropyl trimethoxysilane; Vinyltrimethoxysilane, vinyltriethoxysilane, gamma-methacryloyl oxypropyl methyl dimethoxysilane, vinyl type unsaturation group content Silang [ such as gamma-AKURO yloxy propylmethyl triethoxysilane, ]: --- containing halogen Silang [ such as gamma-chloropropyltrimethoxysilane, ]: --- isocyanurate silanes, such as tris(trimethoxysilyl) isocyanurate, can be mentioned. Amino modifying silyl polymer which is the derivative which denaturalized these. Silanizing amino polymer, an unsaturation aminosilane complex, a phenylamino long chain alkyl silane, amino silanizing silicone, a block isocyanate silane, silanizing polyester, etc. can be used as a silane coupling agent.

[0130]A silane coupling agent used for this invention is usually used in 0.1-20 copies to 100 copies of crosslinkable-silyl-groups content vinyl-base polymers. It is preferred to use it in 0.5-10 copies especially. An effect of a silane coupling agent added by hardenability constituent of this invention, Various adherends, i.e., glass, aluminum, stainless steel, zinc, When it uses for organic group material, such as inorganic substrates, such as copper and mortar, vinyl chloride, an acrylic, polyester, polyethylene, polypropylene, polycarbonate, a remarkable adhesive improvement effect is shown under non primer conditions or priming conditions. When it is used under non primer conditions, especially an effect of improving an adhesive property over various adherends is remarkable. [0131]Especially as examples of an adhesive property other than a silane coupling agent, although not limited, an epoxy resin, phenol resin, sulfur, alkyl titanate, aromatic polyisocyanate, etc. are mentioned, for example. [0132]The above-mentioned adhesive grant agent may be used only by one kind, and may carry out two or more kind mixing use. These adhesive property grant agent can improve an adhesive property over adherend by adding. Although limitation in particular is not carried out, in order to raise an adhesive property and an adhesive property [ especially as opposed to metal covering sides, such as an oil pan mechanism, ], it is preferred to use a silane coupling agent together 0.1 to 20 weight section also in the above-mentioned adhesive grant agent.

[0133]A kind and an addition of an adhesive grant agent can be chosen with a kind of Y of a vinyl-base polymer expressed with the general formula (1) and (6) of this invention, or the number of a, and can control hardenability, a mechanical physical property, etc. of this invention according to the purpose or a use. Since especially hardenability and elongation are influenced, cautions are required for the selection.

Various plasticizers may be used for a hardenability constituent of <plasticizer> this invention if needed. Since elongation of a hardened material can be enlarged or a lot of fillers can be mixed if it is used, using together with a filler which mentions a plasticizer later, it becomes more advantageous,

but it must not necessarily add. Although not limited especially as a plasticizer, for the purpose, such as adjustment of physical properties, and regulation of description. For example, dibutyl phthalate, diheptylphthalate, di(2-ethylhexyl) phthalate, Phthalic ester, such as butylbenzyl phthalate; Dioctyl adipate, Non-aromatic dibasic acid esters, such as dioctyl sebacate, dibutyl sebacate, and succinic acid isodecyl; Butyl oleate, Aliphatic series ester species, such as acetyl RISHIRI Norian acid methyl; Diethylene glycol dibenzoate, Ester species of polyalkylene glycols, such as triethylene glycol dibenzoate and pentaerythritol ester; Triethyl phosphate, phosphoric ester [ such as tributyl phosphate, ]: --- trimellitic acid ester species: --- polystyrene [ such as polystyrene and Poly alpha-methylstyrene ]: --- polybutadiene. Hydrocarbon system oil; process oil, such as polybutene, polyisobutylene, butadiene acrylonitrile, polychloroprene; chlorinated paraffin; alkyl diphenyl, and partially-hydrogenated terphenyl; A polyethylene glycol, a polypropylene glycol, A hydroxyl group of polyether polyol, such as polytetramethylene glycol, and these polyether polyol An ester group. Polyether, such as a derivative changed into an ether group etc.; Epoxidized soybean oil, Epoxy plasticizers, such as epoxy stearic acid benzyl; Sebacic acid, Dibasic acid and ethylene glycol, such as adipic acid, azelaic acid, and phthalic acid; A diethylene glycol, triethylene glycol, propylene glycol, The polyester plasticizers obtained from dihydric alcohol, such as dipropylene glycol; the vinyl-base polymers which are produced by polymerizing by various methods in vinyl system monomers including an acrylic plasticizer are mentioned.

[0134]A polymeric plasticizer which is a polymer of the number average molecular weights 500-15000 especially, While being able to adjust mechanical characteristics, such as tensile strength of a hardened material produced by hardening viscosity of this hardenability constituent, slump nature, and this constituent by adding, and elongation, As compared with a case where a low molecule plasticizer which is a plasticizer which does not contain a polymer component in a molecule is used, early physical properties are maintained over a long period of time, and drying property (it is also called paintwork) at the time of applying an alkyl paint to this hardened material can be improved. Although limitation is not carried out, even if this polymeric plasticizer has a functional group and it does not have it, it is not cared about.

[0135]Above, although number average molecular weights of a polymeric plasticizer were indicated to be 500-15000, they are 800-10000 preferably and are 1000-8000 more preferably. If a molecular weight is too low, a plasticizer can flow out temporally by heat or a rainfall, early physical properties cannot be maintained over a long period of time, and alkyl paintwork cannot be improved. If a molecular weight is too high, viscosity will become high and workability will worsen.

[0136]Among these polymeric plasticizers, a vinyl-base polymer and a thing to dissolve are preferred. A heat-resistant point to compatibility and weatherability, and a vinyl-base polymer are especially preferred. Also in a vinyl-base polymer, an acrylic polymer is preferred (meta) and an acrylic polymer is still more preferred. The synthetic method of this acrylic polymer can mention what is obtained by solution polymerization from the former, solventless type acrylic polymer, etc. Since the latter acrylic plasticizer is produced without a solvent or a chain transfer agent with elevated-temperature continuous polymerization method (USP4414370, JP 59-6207A, JP 5-58005B, JP 1-313522A, USP5010166), it is more preferred for the purpose of this invention. Although not limited especially as the example, Toagosei article UP series etc. are mentioned (refer to industrial material October, 1999 item). Of course, a living-radical-polymerization method can also be mentioned as other synthetic methods. According to this method, molecular weight distribution of that polymer is narrow, and it is desirable from hypoviscosity-izing being possible, and also an atom-transfer-radical-polymerization method is more preferred, but it is not limited to this.

[0137]Although molecular weight distribution in particular of a polymeric plasticizer is not limited, a narrow thing is preferred and less than 1.8 are preferred. 1.7 or less are more preferred, in addition, 1.6 or less are preferred, 1.5 or less are still more preferred, 1.4 especially or less are preferred, and 1.3 or less are the most preferred.

[0138]A plasticizer containing the above-mentioned polymeric plasticizer is not necessarily needed, although it may be used alone and two or more sorts may be used together. A low molecule plasticizer may be further used together in the range which does not have an adverse effect on physical properties using a polymeric plasticizer depending on necessity.

[0139]These plasticizers can also be blended at the time of polymer manufacture.

[0140]Although the amount of [ in case used of using a plasticizer ] is not limited, it is 20 to 100

weight section still more preferably ten to 120 weight section preferably five to 150 weight section to vinyl-base polymer 100 weight section. In less than five weight sections, if an effect as a plasticizer stops being revealed and 150 weight sections are exceeded, mechanical strength of a hardened material runs short.

Various fillers may be used for a hardenability constituent of <filler> this invention if needed. Although not limited, especially as a filler Wood flour, pulp, a cotton chip, Asbestos, glass fiber, carbon fiber, mica, walnut shell powder, chaff powder, graphite, diatomite, clay, and silica (fumed silica and sedimentation nature silica.) Crystalline silica, fused silica, dolomite, a silicic acid anhydride, hydrous silicic acids, etc., A reinforcing filler like carbon black; Heavy calcium carbonate, colloid calcium carbonate, Magnesium carbonate, diatomite, calcination clay, clay, talc, titanium oxide, Bentonite, organic bentonite, ferric oxide, a red oxide, aluminum impalpable powder, Fillers, such as the Flint powder, a zinc oxide, an active white, zinc dust, zinc carbonate, and a milt balloon; fibrous fillers, such as asbestos, glass fiber and a glass filament, carbon fiber, the Kevlar textiles, and a polyethylene fiber, etc. are mentioned.

[0141]Among these fillers, sedimentation nature silica, fumed silica, crystalline silica, fused silica, dolomite, carbon black, calcium carbonate, titanium oxide, talc, etc. are preferred.

[0142]To obtain a hardened material with high intensity with these fillers especially. A filler mainly chosen from fumed silica, sedimentation nature silica, a silicic acid anhydride, hydrous silicic acids, carbon black, surface treatment detailed calcium carbonate, crystalline silica, fused silica, calcination clay, clay, an active white, etc. can be added. specific surface area (based on a BET adsorption process) especially — more than  $50 \text{ m}^2/\text{g}$  — usually —  $50\text{--}400 \text{ m}^2/\text{g}$  — silica of the shape of end of superfines about  $100\text{--}300 \text{ m}^2/\text{g}$  is preferably preferred. Silica by which canal processing of the surface was beforehand carried out with organic silicon compounds, such as an organosilane, the ORGANO silazane, a JIORUGANO cyclopolyloxane, is still more preferred.

[0143]Especially as a more concrete example of a high silica system filler of reinforcement nature, although not limited, Aerosil of Japanese Aerosil which is one of the fumed silica, Nipsil of a Japanese silica company industry which is one of the sedimentation method silica, etc. are mentioned.

[0144]When elongation wants to obtain a hardened material which is size with low strength, a filler mainly chosen from titanium oxide, calcium carbonate, talc, ferric oxide, a zinc oxide, a milt balloon, etc. can be added. Generally, when specific surface area of calcium carbonate is small, an improvement effect of breaking strength of a hardened material, elongation after fracture, an adhesive property, and a weathering adhesive property is not sometimes enough. An improvement effect of breaking strength of a hardened material, elongation after fracture, an adhesive property, and a weathering adhesive property becomes larger, so that a value of specific surface area is large.

[0145]It is more desirable for calcium carbonate to have performed a surface treatment using a finishing agent. When surface treatment calcium carbonate is used, as compared with a case where calcium carbonate which has not carried out a surface treatment is used, the workability of a constituent of this invention is improved and it is thought that an improvement effect of the adhesive property of this hardenability constituent and a weathering adhesive property improves more. As the aforementioned finishing agent, various coupling agents, such as organic matters, such as fatty acid, fatty acid soap, and fatty acid ester, various surface-active agents, and a silane coupling agent, a titanate coupling agent, are used. Although not limited to below, as an example Fatty acid, such as caproic acid, caprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, and oleic acid. Salts, such as sodium of these fatty acid and potassium, and alkyl ester of these fatty acid are mentioned. As an example of a surface-active agent, polyoxyethylene-alkyl-ether sulfate ester, long chain alcoholic sulfate ester, etc. Sulfate ester type anionic surfactants, such as those sodium salt and potassium salt, Alkylbenzene sulfonic acid, alkyl naphthalene sulfonic acid, paraffin sulfonic acid, alpha olefin sulfonic acid, alkyl sulfosuccinic acid, etc. sulfonic acid type anionic surfactants, such as those sodium salt and potassium salt, etc. are mentioned. As for a throughput of this finishing agent, it is preferred to process in 0.1 to 20% of the weight of the range. When a throughput is less than 0.1 % of the weight, an improvement effect of weight of the range. When a throughput is less than 0.1 % of the weight, an improvement effect of workability, an adhesive property, and a weathering adhesive property is not sometimes enough and 20 % of the weight is exceeded, the storage stability of this hardenability constituent may fall.

[0146]Although limitation in particular is not carried out, when using calcium carbonate, and it

expects especially improvement effects, such as the thixotropy of a compound, breaking strength of a hardened material, elongation after fracture, an adhesive property, and a weathering adhesive property, it is preferred to use colloid calcium carbonate.

[0147]On the other hand, although it may add for the purpose of hypoviscosity-izing of a compound, increase in quantity, a cost cut, etc., heavy calcium carbonate can use the following if needed, when using this heavy calcium carbonate.

[0148]With heavy calcium carbonate, natural chalk (chalk), marble, limestone, etc. are ground and processed mechanically. Although there are a dry method and wet process about a grinding method, it is common for a wet-milling article not to be desirable in order to worsen the storage stability of a hardenability constituent of this invention in many cases. Heavy calcium carbonate serves as a product which has various mean particle diameter by a classification. Although not limited in particular, in expecting an improvement effect of breaking strength of a hardened material, elongation after fracture, an adhesive property, and a weathering adhesive property, The following [ $50 \text{ m}^2/\text{g}$ ] have [ $\text{more than } 1.5 \text{ m}^2/\text{g}$ ] a preferred value of specific surface area, below  $50 \text{ m}^2/\text{g}$  is [ $\text{more than } 2 \text{ m}^2/\text{g}$ ] still more preferred, below  $50 \text{ m}^2/\text{g}$  is [ $\text{more than } 2.4 \text{ m}^2/\text{g}$ ] more preferred, and below  $50 \text{ m}^2/\text{g}$  especially is [ $\text{more than } 3 \text{ m}^2/\text{g}$ ] preferred. When specific surface area is less than  $1.5 \text{ m}^2/\text{g}$ , the improvement effect is not sometimes enough. Of course, it is not this limitation when aiming only at a case where viscosity is only reduced, or increase in quantity.

[0149]A value of specific surface area means measured value by an air permeability method (how to determine specific surface area from the permeability of air to a granular material packed bed.) performed according to JIS K 5101 as a measuring method. As measuring equipment, it is preferred to use Shimadzu specific surface area measuring instrument SS-100 type.

[0150]These fillers may be independently used together the purpose and if needed, and may use two or more sorts together. Although limitation in particular is not carried out, if a value of specific surface area combines heavy calcium carbonate and colloid calcium carbonate more than  $1.5 \text{ m}^2/\text{g}$  if needed, it suppresses a rise of viscosity of a compound moderately and an improvement effect of breaking strength of a hardened material, elongation after fracture, an adhesive property, and a weathering adhesive property can expect it very much, for example.

[0151]As for an addition in a case of using a filler, it is preferred to use a filler in the range of five to 1000 weight section to vinyl-base polymer 100 weight section, it is more preferred to use it in the range of 20 to 500 weight section, and it is preferred especially to use it in the range of 40 to 300 weight section. When loadings are less than five weight sections, an improvement effect of breaking strength of a hardened material, elongation after fracture, an adhesive property, and a weathering adhesive property is not sometimes enough, and when 1000 weight sections are exceeded, the workability of this hardenability constituent may fall. A filler may be used alone and may be used together two or more sorts.

A minute empty capsid may be used together to these reinforcing fillers for the purpose of attaining a weight saving and low cost-ization, without causing a <minute empty capsid> and also a big fall of physical properties.

[0152]Such a very small empty capsid (henceforth a balloon), Although limitation in particular is not carried out, a hollow body by which 500 micrometers or less of diameters were preferably constituted still more preferably from material of minerals of 200 micrometers or less or quality of organicity 1 mm or less is mentioned as indicated on "state-of-the-art of a functional filler" (CMC). It is preferred that true specific gravity uses especially a very small hollow body which is below  $1.0 \text{ g/cm}^3$ , and also it is preferred to use a very small hollow body which is below  $0.5 \text{ g/cm}^3$ .

[0153]As said inorganic system balloon, can illustrate a silicic acid system balloon and a non-silicic acid system balloon, and on a silicic acid system balloon. A milt balloon, perlite, glass balloons, a silica balloon, fly ash balloons, etc. can illustrate an alumina balloon, a zirconia balloon, a carbon balloon, etc. on a non-silicic acid system balloon. A win light by [as an example of these inorganic system balloons / as a milt balloon] IJIOHI Chemicals, Nippon Sheet Glass KARUN as a Sanki Engineering balloons / as a milt balloon, A Sumitomo 3M cell star Z-28, MICRO BALLOON made from EMERSON&CUMING, CELAMIC GLASSMODULES made from PITTSBURGE CORNING, AS GLASS BUBBLES made from 3M, and a silica balloon as Asahi Glass Q-CEL, Taiheyo Cement E-SPHERES, and fly ash balloons, CEROSPHERES made from PFAMARKETING, FILLITE made from FILLITE U.S.A.

HOLLOW ZIRCONIUM SPHEES of a product made from ZIRCOA as Showa Denko BW as an alumina balloon, and a zirconia balloon, KUREKASU fair made from the Kureha chemicals and product car boss fair made from GENERAL TECHNOLOGIES are marketed as a carbon balloon.

[0154]A balloon of thermosetting resin and a balloon of thermoplastics can be illustrated as said organic system balloon. On a thermosetting balloon, a phenol balloon, an epoxy balloon, and a urea balloon can illustrate a saran balloon, a polystyrene balloon, a polymethacrylate balloon, a polyvinyl alcohol balloon, and a styrene acrylic balloon at a thermoplastic balloon. A balloon of thermoplastics which constructed the bridge can also be used. A balloon after foaming may be sufficient, and a balloon here is made to foam, after blending a thing containing a foaming agent, and is good also as a balloon.

[0155]Union Carbide UCAR and PHENOLIC MICROBALLOONS as a phenol balloon as an example of these organic system balloons, ECCOSPHERES of a product made from EMERSON&CUMING as an epoxy balloon, ECCOSPHERES VF-O of a product made from EMERSON&CUMING as a urea balloon, SARAN MICROSPHERES of a product made from DOW CHEMICAL as a saran balloon, Expancel made from a Japanese filament, a Matsumoto Yushi-Seiyaku Matsumoto microsphere, DYLITE EXPANDABLE POLYSTYRENE of a product made from ARCO POLYMERS as a polystyrene balloon, Japan Synthetic Rubber 863 [SX] (P) are marketed by EXPANDABLE POLYSTYRENE BEADS made from BASF WYANDOTE, and constructed type styrene acrylic acid balloon of a bridge.

[0156]The above-mentioned balloon may be used alone, and two or more kinds may be mixed and it may be used. The surface of these balloons Fatty acid, fatty acid ester, rosin, What was processed in order to improve dispersibility and the workability of a compound by rosin acid lignin, a silane coupling agent, titanium coupling agent, aluminum cup ring agent, a polypropylene glycol, etc. can be used. Without spilling pliability, and elongation and intensity among physical properties at the time of stiffening a compound, these balloons are used in order to carry out a weight saving and to cut down the cost.

[0157]Although content in particular of a balloon is not limited, it can be preferably used in 0.1-30 copies still more preferably 0.1-50 copies to vinyl-base polymer 100 weight section. A fall of tensile strength may be accepted among mechanical characteristics when an effect of a weight saving is small in less than 0.1 copy and this quantity stiffens this compound in 50 or more copies. When specific gravity of a balloon is 0.1 or more, 5-30 copies are still more preferably preferred 3-50 copies.

A physical-properties regulator which adjusts the tractive characteristics of a hardened material generated if needed to a hardenability constituent of <physical-properties regulator> this invention may be added.

[0158]Although not limited especially as a physical-properties regulator, for example Methyl trimethoxysilane, Alkyl alkoxy silane, such as dimethyldimethoxysilane, trimethylmethoxysilane, and n-propyltrimethoxysilane; Dimethylidi iso propenoxysilane, Alkyl iso propenoxysilane, such as methyl-TORISO propenoxysilane and gamma-glycidoxy propylmethyl JISO propenoxysilane, gamma-glycidoxy propyl methylmethoxysilane, gamma-glycidoxypropyltrimethoxysilane, Vinyltrimethoxysilane, vinylidimethylmethoxysilane, gamma-aminopropyl trimethoxysilane, The alkoxy silane; silicone varnishes which have functional groups, such as N-(beta-aminoethyl) aminopropyl methyl dimethoxysilane, gamma-mercaptopropyltrimethoxysilane, and gamma-mercaptopropylmethyl dimethoxysilane; polysiloxanes are mentioned. By using said physical-properties regulator, hardness when stiffening a constituent of this invention is raised, or hardness is lowered and elongation can be taken out. The above-mentioned physical-properties regulator may be used independently, and may be used together two or more sorts.

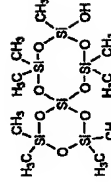
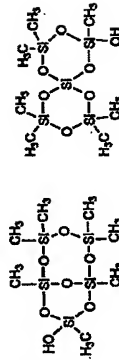
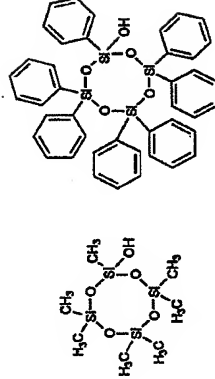
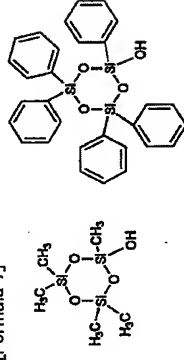
A silanol content compound may be added if needed [such as changing the physical properties of a hardened material into a hardenability constituent of <silanol content compound> this invention, ]. A silanol content compound means a compound which has one silanol group in intramolecular, and/or a compound which can generate a compound which has one silanol group in intramolecular by reacting to moisture. These may use only one side and may use both compounds simultaneously.

[0159]A compound which has one silanol group in intramolecular which is one of the silanol content compounds,  $(CH_3)_3SiOH$  which it was not limited but were especially below,

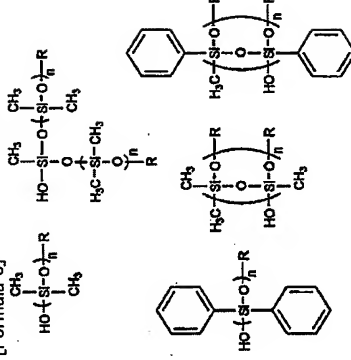


$(C_6H_{11})_3SiOH, (C_6H_9)_3SiOH, (C_6H_5)_3SiOH, (C_6H_5)_2Si(CH_3)_2Si(CH_3)_2OH, Si(C_6H_5)_2(OH)_2, (C_6H_5)_2Si(C_2H_5)_2Si(C_2H_5)_2OH, C_6H_5CH_2Si(C_2H_5)_2OH, C_6H_5CH_2Si(CH_3)_2OH$  (however, the above-mentioned  $C_{6in}$  formula  $H_5$  shows a phenyl group, and  $C_{10}H_7$  shows a naphthyl group.)

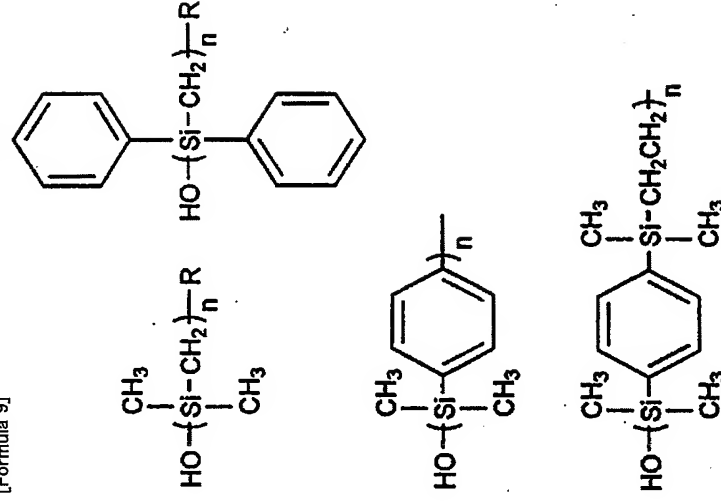
A compound which can express with  $_3SiOH$  (it corrects and Rin formula" is substitution, an unsubstituted alkyl group, or an aryl group same or of a different kind) like \*\* (R"), [0160]



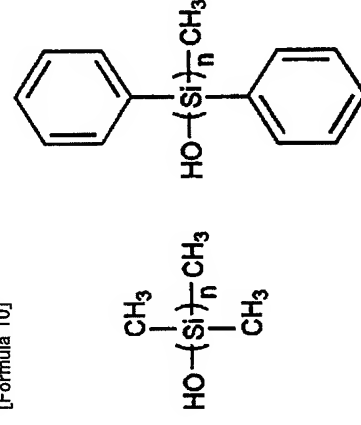
The annular polysiloxane compound containing a silanol group like \*\*, [0161]



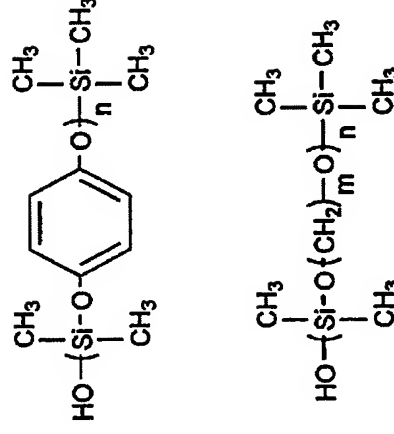
The chain polysiloxane compound containing a silanol group like \*\*, [0162]  
[Formula 9]



The compound which the silanol group combined with the polymer terminals which a main chain like \*\* becomes from silicon and carbon, [0163]  
[Formula 10]



The compound which the silanol group combined with a polysilane main chain terminal like \*\*, [0164]  
[Formula 11]



The compound etc. which the silanol group combined with the polymer terminals which a main chain like \*\* becomes from silicon, carbon, and oxygen can be illustrated. Among these, the compound expressed with a following general formula (45) is preferred.  
(R<sup>58</sup>)<sub>3</sub>SiOH (45)

(R<sup>58</sup>) shows the univalent hydrocarbon group of the carbon numbers 1-20 among a formula.) Two or more R<sup>58</sup> may be the same, or may differ.

R<sup>27</sup> has a methyl group, an ethyl group, a vinyl group, a t-butyl group, and a preferred phenyl group, and its methyl group is still more preferred.

[0165] Especially, acquisition is easy and <sub>3</sub>SiOH with the point of an effect to a small (CH<sub>3</sub>)<sub>3</sub> molecular weight, etc. are preferred.

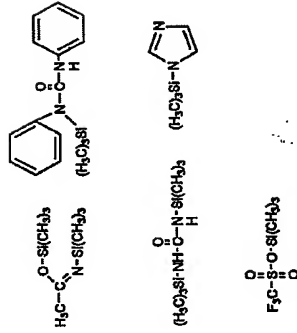
[0166] By reacting to a siloxane bond generated according to crosslinkable silyl groups of a vinyl-base polymer, or bridge construction, a compound which has one silanol group in the above and intramolecular decreases the number of points constructing a bridge, and is presumed to have given pliability to a hardened material. A compound which can generate a compound which has one silanol group in intramolecular by reacting to moisture which is one of the ingredients of this invention, Although not limited in particular, a compound by which a compound (hydrolysis product) which has one silanol group is expressed with the above-mentioned general formula (45) to intramolecular which reacts to moisture and is generated is preferred. For example, although not necessarily limited especially, the following compound can be mentioned in addition to a compound expressed with a general formula (46) which is mentioned later.

[0167] A N,O-bis(trimethylsilyl)acetamide, N-(trimethylsilyl) acetamide, A bis(trimethylsilyl) trifluoroacetamide, N-methyl-N-trimethylsilyl trifluoroacetamide, Screw trimethylsilyl urea, an N-(t-butyltrimethylsilyl) N-methyltrifluoroacetamide, (N and N-dimethylamino) Trimethylsilane, trimethylsilane (N and N-diethylamino), Hexamethyldisilazane, 1, 1 and 3, 3-tetramethyl disilazane, N-(trimethylsilyl) imidazole, trimethylsilyl trifluoromethane sulfonate, Trimethylsilyl phenoxide, a trimethylsilyl ghost of n-octanol, A trimethylsilyl ghost of 2-ethylhexanol, a tris (trimethylsilyl) ghost of glycerin, A tris (trimethylsilyl) ghost of trimethylolpropane, a tris (trimethylsilyl) ghost of pentaerythritol, A tetra (trimethylsilyl) ghost of pentaerythritol, (CH<sub>3</sub>)<sub>3</sub>SiNHSi(CH<sub>3</sub>)<sub>3</sub> (CH<sub>3</sub>)<sub>3</sub>SiNSi

(CH<sub>3</sub>)<sub>2</sub>, [0168]

[Formula 12]





Although \*\* can use it conveniently, from the quantity of the content silanol group of a hydrolysis product, especially  $(CH_3)_3SiNH(CH_2)_3$  is preferred.

[0169] Although the compound in particular that can generate the compound which has one silanol group in intramolecular by reacting to the moisture which is furthermore one of the ingredients of this invention is not limited, its compound expressed with a following general formula (46) in addition to the above-mentioned compound is preferred.

(R<sup>58</sup>)<sub>n</sub> R<sup>59</sup> (SiO) (46)

(R<sup>58</sup>) is the same as that of what was mentioned above among a formula.) Or n shows the basis except all the active hydrogen. [ positive number ] [ R<sup>59</sup> ] [ from active hydrogen containing compounds ]

R<sup>58</sup> has a methyl group, an ethyl group, a vinyl group, t-butyl group, and a preferred phenyl group, and its methyl group is still more preferred. (R<sup>59</sup>) A Si group has especially a preferred trimethylsilyl group in which all three R<sup>58</sup> are methyl groups. As for n, 1-5 are preferred.

[0170] Although not limited especially as active hydrogen containing compounds used as the origin of the above-mentioned R<sup>59</sup>, For example, methanol, ethanol, n-butanol, t-butanol, n-octanol, 2-ethylhexanol, benzyl alcohol, Ethylene glycol, a diethylene glycol, a polyethylene glycol, Propylene glycol, dipropylene glycol, a polypropylene glycol, A propanediol, tetramethylene glycol, polytetramethylene glycol, Alcohols, such as glycerin, trimethylolpropane, and pentaerythritol, Phenol, Phenols, such as cresol, bisphenol A, and hydroquinone; Formic acid, Acetic acid, propionic acid, lauric acid, palmitic acid, stearic acid, behenic acid, Acrylic acid, methacrylic acid, oleic acid, linolic acid, linolenic acid, Sorbic acid, malonic acid, succinic acid, adipic acid, maleic acid, Amino acids, such as carboxylic acid; ammonia; methylamines, such as benzoic acid, phthalic acid, terephthalic acid, and trimellitic acid, dimethylamine, ethylamine, diethylamine, n-butylamine, and imidazole; Acid amides, such as an acetamide and benzamide. Urea, such as urea and a N,N'-diphenylurea; ketone, such as acetone, an acetylacetone, and 2,4-heptadione, is mentioned.

[0171] A compound which can generate a compound which has one silanol group in intramolecular by reacting to moisture expressed with the above-mentioned general formula (46). To for example, above-mentioned active hydrogen containing compounds etc. Although it can obtain by making a compound which has a basis which can react to active hydrogen, such as a halogen atom, with a Si group called sillation reagents, such as trimethylsilyl chloride and dimethyl(t-butyl)chloride (R<sup>58</sup>) react. It is not limited to these (however, R<sup>58</sup> is the same as that of what was mentioned above.).

[0172] When a compound expressed with the above-mentioned general formula (46) is illustrated concretely, allyloxy trimethylsilane, A N,O-bis(trimethylsilyl)acetamide, N-(trimethylsilyl) acetamide, A bis(trimethylsilyl)trifluoroacetamide, N-methyl-N-trimethylsilyl trifluoroacetamide, Screw trimethylsilyl urea, an N-(t-butyl)dimethylsilyl N-methyltrifluoroacetamide, (N and N-dimethylamino) Trimethylsilane, trimethylsilane (N and N-diethylamino), Hexamethyldisilazane, 1, 1 and 3, 3-tetramethyl disilazane, N-(trimethylsilyl) imidazole, trimethylsilyl trifluoromethane sulfonate, Trimethylsilyl phenoxide, a trimethylsilyl ghost of n-octanol, A trimethylsilyl ghost of 2-ethylhexanol, a tris (trimethylsilyl) ghost of glycerin, Although a tris (trimethylsilyl) ghost of trimethylolpropane, a tris

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(trimethylsilyl) ghost of pentaerythritol, a tetra (trimethylsilyl) ghost of pentaerythritol, etc. are mentioned, it is not limited to these. These may be used independently and may use two or more sorts together.

[0173] A compound which can express with general formula (R<sup>60</sup>)<sub>3</sub>SiO (R<sup>61</sup>O) (Z) CH<sub>3</sub>O(CH<sub>2</sub>)CH(CH<sub>3</sub>) O<sub>5</sub>Si(CH<sub>3</sub>)<sub>3</sub> (CH<sub>3</sub>)<sub>3</sub>SiO(CH<sub>2</sub>)CH(CH<sub>3</sub>) O<sub>5</sub>Si(CH<sub>3</sub>)<sub>3</sub> (CH<sub>3</sub>)<sub>3</sub>SiO(CH<sub>2</sub>)CH(CH<sub>3</sub>) O<sub>5</sub>Si(CH<sub>3</sub>)<sub>3</sub> (among a formula) 1-6, and sxt are five or more, as for R<sup>60</sup>, a divalent hydrocarbon group of the carbon numbers 1-8, s, and t of a univalent hydrocarbon group substitution same or of a different kind or unsubstituted or a hydrogen atom, and R<sup>61</sup> are positive integers, and, as for s, Z is an organic group of 1 - 6 value.

\*\*\* — it can be used conveniently. These may be used independently and may use two or more sorts together.

[0174] In a compound which can generate a compound which has one silanol group in intramolecular by reacting to moisture, Active hydrogen containing compounds generated after hydrolysis at a point which does not have an adverse effect on storage stability, weatherability, etc. have phenols, acid amides, and preferred alcohols, and its phenols and alcohols whose active hydrogen containing compounds are hydroxyl groups are still more preferred.

[0175] In the above-mentioned compound, a N,O-bis(trimethylsilyl)acetamide, N-(trimethylsilyl) acetamide, trimethylsilyl phenoxide, A trimethylsilyl ghost of n-octanol, a trimethylsilyl ghost of 2-ethylhexanol, A tris (trimethylsilyl) ghost of glycerin, a tris (trimethylsilyl) ghost of trimethylolpropane, a tris (trimethylsilyl) ghost of pentaerythritol, a tetra (trimethylsilyl) ghost of pentaerythritol, etc. are preferred.

[0176] A compound which can generate a compound which has one silanol group in intramolecular generates a compound which has one silanol group in intramolecular by reacting to moisture after the time of hardening, or hardening by reacting to this moisture at the time of storage. Thus, by reacting to a siloxane bond generated as mentioned above according to crosslinkable silyl groups of a vinyl-base polymer, or bridge construction, a compound which has one silanol group in generated intramolecular decreases the number of points constructing a bridge, and is presumed to have given pliability to a hardened material.

[0177] An addition of a silanol content compound can be suitably adjusted according to the expected physical properties of a hardened material. The silanol content compound can carry out 0.5-10 weight-section addition still more preferably 0.3 to 20 weight section preferably 0.1 to 50 weight section to vinyl-base polymer 100 weight section. In less than 0.1 weight sections, if the addition effect does not show up but 50 weight sections are exceeded, bridge construction will become insufficient and intensity and a gel fraction of a hardened material will fall too much.

[0178] It may not be limited, but may add at the time of manufacture of a vinyl-base polymer, and especially the stage to add a silanol content compound to a vinyl-base polymer may be added at the time of production of a hardenability constituent.

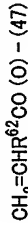
In a hardenability constituent of <thixotropic grant agent (lappet inhibitor)> this invention, a lappet is prevented if needed, and in order to improve workability, a thixotropic grant agent (lappet inhibitor) may be added.

[0179] Although not limited especially as a lappet inhibitor, metallic soap, such as polyamide waxes, hydrogenation castor oil derivative; calcium stearate, aluminum stearate, and barium stearate, is mentioned, for example. These thixotropic grant agent (lappet inhibitor) may be used independently, and may be used together two or more sorts.

In a hardenability constituent of <photorealist substance> this invention, a photorealist substance may be added if needed. By operation of light, molecular structure causes a chemical change for a short time, and a photorealist substance produces physical-properties change of hardening etc. for it. By adding this photorealist substance, adhesiveness on the surface of a hardened material at the time of stiffening a hardenability constituent (it is also called a residual tack) can be reduced. Although this photorealist substance is a substance which can be hardened by hitting light, a typical photorealist substance is a substance which can be stiffened by settling on a position (near a window) to which an indoor day corresponds, for example at a room temperature for one day. Although many things, such as a constituent containing an organic monomer, oligomer, resin, or them, are known by this kind of compound and that kind in particular is not limited to it, an unsaturation acrylic compound,

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polycinnamic acid vinyl, or azide-ized resin is mentioned, for example.  
 [0180]Unsaturation acrylic compounds are monomers and oligomer which have an unsaturation group expressed with a following general formula (47), or these mixtures.



R<sup>62</sup> shows hydrogen, an alkyl group of the carbon numbers 1-10, an aryl group of the carbon numbers 6-10, or an aralkyl group of the carbon numbers 7-10 among a formula.

[0181]As an unsaturation acrylic compound, specifically, Ethylene glycol, glycerin, trimethylolpropane, pentaerythritol, The acrylic ester (meta) of low-molecular-weight alcohols, such as neopentyl alcohol, Bisphenol A, The acrylic ester (meta) of alcohols which denaturalized acid or the above-mentioned low-molecular-weight alcohol, such as isocyanuric acid, etc. by ethylene oxide or propylene oxide; Polyether polyol to which a main chain has a hydroxyl group at the end by polyether, Polymeric polyol obtained when a main chain carries out the radical polymerization of the vinyl system monomer in polyol which is polyether, Polyester polyol to which a main chain has a hydroxyl group at the end with polyester, A main chain is a vinyl system or (meta) an acrylic polymer, Acrylic ester (meta), such as polyol which has a hydroxyl group in a main chain; Epoxy acrylate system oligomer, polyol obtained by making an epoxy resin and acrylic acid (meta), such as a bisphenol A type and a novolac type, react, Urethane acrylate system oligomer etc. which have a urethane bond and (meta) an acrylic group are mentioned into a chain obtained by making polyisocyanate, hydroxyl group content (meta) acrylate, etc. react.

[0182]Polycinnamic acid vinyl is the photopolymers which use a cinnamoyl group as a sensitization group, and a polycinnamic acid vinyl system derivative of many besides what esterified polyvinyl alcohol with cinnamic acid is mentioned.

[0183]Azide-ized resin is known as a photopolymer which uses an azido group as a sensitization group, usually --- a rubber sensitizing solution etc. which added an azide compound as a sensitizing agent have detailed a "photopolymer" (from Showa 47(1972) March 17 publication, printing society publication part issue, and 93 pages - 106 pages to 117page-) illustration --- these --- a sensitizer can be used, being able to mix and adding [ it can be independent, or ] if needed.

[0184]An unsaturation acrylic compound is preferred for a Reason for being easy to deal with it in the above-mentioned photoresist substance.

[0185]As for a photoresist substance, it is preferred to carry out 0.01-20 weight-section addition to vinyl-base polymer 100 weight section. In less than 0.01 weight sections, when an effect is small and 20 weight sections are exceeded, an adverse effect to physical properties may come out. Addition of accelerators, such as sensitizers, such as ketone and a nitro compound, and amines, may heighten an effect.

In a hardenability constituent of <air-oxidation hardenability substance> this invention, an air-oxidation hardenability substance may be added if needed. An air-oxidation hardenability substance is a compound which has an unsaturation group which can carry out bridge construction hardening by oxygen in the air. By adding this air-oxidation hardenability substance, adhesiveness on the surface of a hardened material at the time of stiffening a hardenability constituent (it is also called a residual tack) can be reduced. An air-oxidation hardenability substance in this invention is a substance which can be hardened by making air contact, and, more specifically, has the character which reacts to oxygen in the air and is hardened. A typical air-oxidation hardenability substance can be stiffened by settling indoors for one day, for example in the air.

[0186]Various alkyd resins produced by denaturalizing drying oil; these drying oil, such as tung oil and linseed oil, as an air-oxidation hardenability substance, for example; An acrylic polymer which denaturalized with drying oil, Various denaturation things (a mallein-ized denaturation thing, a boiled oil denaturation thing, etc.) of a polymer, a copolymer and also this polymer of C5 - C8 diene, or a copolymer, etc. are mentioned as an example in epoxy-system-resin and silicone resin; 1,2-polybutadiene and 1,4-polybutadiene. Especially among these, a liquid object (liquefied diene system polymer) of tung oil and the diene system polymers and its denaturation thing are preferred.

[0187]As an example of the above-mentioned liquefied diene system polymer, butadiene, chloroprene, Diene series, such as isoprene and 1,3-pentadiene, a polymerization or a liquefied polymer produced by making carry out copolymerization, Polymers, those various denaturation things, etc. (a mallein-ized denaturation thing, a boiled oil denaturation thing, etc.), such as NBR, SBR, etc. which are produced by making carry out copolymerization of these diene series and the monomers which have

copolymeric, such as acrylonitrile and styrene, so that diene series may serve as a subject, are mentioned. These may be used independently and may use two or more sorts together. Among these liquefied diene series, liquid polybutadiene is preferred.

[0188]An air-oxidation hardenability substance may be used independently and may use two or more sorts together. Concomitant use of a catalyst and a metal drier which promote an oxidation hardening reaction simultaneously with an air-oxidation hardenability substance may heighten an effect. As these catalysts and metal driers, metal salt, amine compounds, etc., such as cobalt naphthenate, lead naphthenate, a naphthenic acid zirconium, octylic acid cobalt, and an octylic acid zirconium, are illustrated.

[0189]As for an air-oxidation hardenability substance, it is preferred to carry out 0.01-20 weight-section addition to vinyl-base polymer 100 weight section. In less than 0.01 weight sections, when an effect is small and 20 weight sections are exceeded, an adverse effect to physical properties may come out.

In a hardenability constituent of <antioxidant> this invention, an antioxidant may be added if needed. An antioxidant is not necessarily limited to these, although various things which various kinds of things are known, were indicated to an "antioxidant handbook" of completion company issue, "degradation, stabilization" (235-242) of the CMC chemicals issue of a polymer material, etc. are mentioned.

[0190]For example, MARK PEP-36, a thioether series of MARK AO-23 grade (all are the products made from the Ade \*\*\*\*\* chemicals above). The Lynn system antioxidants, such as Irgafos38, Irgafos168, and Irgafos-EPQ (all are the Ciba-Geigy Japan make above), etc. are mentioned. Especially, a hindered phenol system compound as shown below is preferred.

[0191]As a hindered phenol system compound, the following can specifically be illustrated. 2,6-di-tert-butyl-4-methyl phenol, 2,6-di-tert-butyl-4-ethylphenol, Mono(or JI or Tori) (alpha methylbenzyl) phenol, 2,2'-methylenebis (4 ethyl-6-tert-butylphenol), 2,2'-methylenebis (4 methyl-6-tert-butylphenol), 4,4'-butyldienebis (3-methyl-6-tert-butylphenol), 4,4'-Thiobis (3-methyl-6-tert-butylphenol), 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amyl hydroquinone, Triethylene glycol bis-[3-(3-t-butyl-5-methyl-4-hydroxyphenyl) propionate], 1,6-hexane \*\*\*\*\* [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], 2,4-bis-(n-octylthio)-6-(4-hydroxy-3,5-di-tert-butylamino)-1,3,5-triazine, pentaerythritol tetraakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], A 2,2'-thio-diethylenescrew [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, N,N'-hexa methylenebis (3,5-di-tert-butyl-4-hydroxy-hydronalium thinner MAMIDO), 3,5-di-tert-butyl-4-hydroxy-benzylphosphonate-diethyl ester, 1,3,5-trimethyl 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl) benzene, Bis(3,5-di-tert-butyl-ethyl 4-hydroxybenzylphosphonate)calcium, Tris-(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 2, 4-2,4-screw [octylthio methyl] o-cresol, N,N'-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionyl] hydrazine, Tris (2,4-di-tert-butylphenyl) phosphite, 2-(5-methyl-2-hydroxyphenyl) benzotriazol, 2-[2-hydroxy-3,5-bis(alpha and alpha-dimethylbenzyl)phenyl]-2H-benzotriazol, 2-(3,5-di-tert-butyl-2-hydroxyphenyl) benzotriazol, A 2-(3-tert-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazole, A 2-(3,5-di-tert-butyl-2-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3,5-di-tert-amyl 2-hydroxyphenyl) benzotriazol, 2-(2'-hydroxy-5-tert-octylphenyl)- Benzotriazol, A condensate with a methyl-3-[3-t-butyl-5-(2H-benzotriazol 2-yl)]-4-hydroxyphenyl propionate polyethylene glycol (molecular weight 300 [ about ]), Hydroxyphenyl benzotriazole derivatives, a 2-(3,5-di-tert-butyl-4-hydroxybenzyl)-2-n-butylmalonic acid screw (1,2,2,6,6-pentamethyl 4-piperidyl), 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxy benzoate etc. are mentioned.

[0192]If it says with a trade name, NOKURAKKU 200, NOKURAKKU M-17, NOKURAKKU SP, NOKURAKKU SP-N, NOKURAKKU NS-5, NOKURAKKU NS-6, NOKURAKKU NS-30, NOKURAKKU 300, NOKURAKKU NS-7, NOKURAKKU DAH (all are the products made from the Ouchi Shinko Chemical industry above), MARK AO-30, MARK AO-40, and MARK AO-50, MARKAO-60, and MARK AO-616, MARK AO-635, MARK AO-658, MARK AO-80, MARK AO-15, MARK AO-18, MARK 328, MARK AO-37 (all are the products made from ADEKAAGASU chemicals above), IRGANOX-245, IRGANOX-259, IRGANOX-565, IRGANOX-1010, IRGANOX-1024, IRGANOX-1035, IRGANOX-1076, IRGANOX-1081, IRGANOX-1098, IRGANOX-1222, IRGANOX-1330, IRGANOX-1425WL (all are the Ciba-Geigy Japan make above), SumilizerGM, Although SumilizerGA-80 (all are the Sumitomo Chemical make above) etc. can be illustrated, it is not limited to these.

[0193]Especially since an antioxidant may be used together with light stabilizer mentioned later, and may demonstrate the effect further by using together and especially its heat resistance may improve, it is preferred. The tinuvin C553 which has mixed an antioxidant and light stabilizer beforehand, the tinuvin B75 (all are the Ciba-Geigy Japan make above), etc. may be used.

[0194]As for the amount of antioxidant used, it is preferred that it is the range of 0.1 to 10 weight section to vinyl-base polymer 100 weight section. There are few effects of an improvement of weatherability at less than 0.1 weight sections, and there is no great difference in an effect and it is economically disadvantageous for it at more than 5 weight copy.

In a hardenability constituent of light stabilizer this invention, light stabilizer may be added if needed. Light stabilizer is not necessarily limited to these, although various things which various kinds of things are known, for example, were indicated to an "antioxidant handbook" of completion company issue, "degradation, stabilization" (235-242) of the CMC chemicals issue of a polymer material, etc. are mentioned.

[0195]Although limitation in particular is not carried out, also in light stabilizer, an ultraviolet ray absorbent's is preferred and specifically, A triazine series like benzotriazol system compounds, such as the tinuvin P, the tinuvin 234, the tinuvin 320, the tinuvin 326, the tinuvin 327, the tinuvin 329, and the tinuvin 213 (all are the Ciba-Geigy Japan make above), or tinuvin 1577 grade, Benzozate system compounds, such as a benzophenone series like CHIMASSORB81 grade and the tinuvin 120 (made by Ciba-Geigy Japan), etc. can be illustrated.

[0196]JA hindered amine system compound is also preferred and such a compound is indicated below. The succinate dimethyl 1-(2-hydroxyethyl)-4-hydroxy-2, 2, and 6, 6-tetramethylpiperidine polycondensation thing. Poly [(6-(1,3,3-tetramethylbutyl) amino-1,3,5-triazine 2,4-diyl) and {(2, 2, 6, and 6-tetramethyl 4-piperidyl) imino}], A N,N-bis(3 aminopropyl)ethylene diamine 2,4-screw [N-butyl-N-(1,2,2,6,6-pentamethyl 4-piperidyl) amino]-6-chloro-1,3,5-triazine condensate, Bis(2,2,6,6-tetramethyl 4-piperidyl)sebacate, succinic acid-bis(2,2,6,6-tetramethyl 4-PIPERIDINYL)ester, etc. are mentioned.

[0197]If it says with a trade name, tinuvin 622LD, the tinuvin 144, CHIMASSORB944LD, CHIMASSORB119flore line and Irgafos168 — (— the above — any — Ciba-Geigy Japan). MARK LA-52, MARK LA-57, MARK LA-62, and MARK LA-67, MARK LA-63, MARK LA-68, MARKLA-82, and MARK LA-87 — (— the above — any —) made from the Ade \*\*\*\*\* chemicals. Although SANORU LS-770, SANORU LS-765, SANORU LS-292, SANORU LS-2826, SANORU LS-1114, SANORU LS-744, SANORU LS-440 (all are the Sankyo make above), etc. can be illustrated, it is not limited to these.

[0198]Since combination of an ultraviolet ray absorbent and a hindered amine system compound may demonstrate an effect more, although limitation in particular is not carried out, it may use together, and using together is sometimes preferred.

[0199]Especially since light stabilizer may use together with an antioxidant mentioned above, and may demonstrate the effect further by using together and especially its weatherability may improve, it is preferred. The tinuvin C553 which has mixed light stabilizer and an antioxidant beforehand, the tinuvin B75 (all are the Ciba-Geigy Japan make above), etc. may be used.

[0200]As for the amount of light stabilizer used, it is preferred that it is the range of 0.1 to 10 weight section to vinyl-base polymer 100 weight section. There are few effects of an improvement of weatherability at less than 0.1 weight sections, and there is no great difference in an effect and it is economically disadvantageous for it at more than 5 weight copy.

In a hardenability constituent of other additive agent this inventions, various additive agents may be added if needed for the purpose of adjustment of the various physical properties of a hardenability constituent or a hardened material. As an example of such an additive, fire retardant, a hardenability regulator, an antiaging agent, radical inhibitor, an ultraviolet ray absorbent, a metal deactivator, anti-ozonant, the Lynn system peroxide decomposition agent, lubricant, paints, a foaming agent, a photo-setting resin, etc. are raised, for example. These various additive agents may be used independently and may use two or more kinds together.

[0201]An example of such an additive is written in each Description of JP,4-69659.B, JP,7-108928.B, JP,63-254149.A, and JP,64-22904.A, for example.

[0202]A hardenability constituent of this invention carries out combination seal preservation of all the combination ingredients beforehand. It may prepare as one component type hardened with humidity in

the after-construction air, ingredients, such as a curing catalyst, a filler, a plasticizer, and water, are separately blended as a hardening agent, and it may adjust as two component types mixed before using this compounding agent and a polymer composition. If two component types are used, colorant can be added at the time of mixing of two ingredients. For example, multiple color-sized correspondence currently demanded from a commercial scene becomes easy, and it is preferred by an object for low rise buildings, etc. that it becomes possible to \*\*\*\*\* by being abundant with the limited stock when a sealing material which doubled with a color of a siding board is provided etc. Colorant will work easily, for example, if paints, a plasticizer, and a thing that mixed and pasted a filler depending on the case are used. A cure rate can be finely tuned by adding a retardant at the time of mixing of two ingredients in a work site.

A hardenability constituent of <hardened material>> <use> this invention, Although limitation is not carried out, sealing materials, such as a structural elastic sealing compound and a sealing material for multiple glass, Electrical insulation materials, such as electric electronic component materials, such as a solar cell rear-face sealing agent, pre-insulation an electric wire, material for cables, A binder, adhesives, elastic adhesives, a paint, powder coatings, a coating material, foam, It is available for various uses, such as a fluid-sealant agent used in a potting agent for electric electrons, a film, a gasket, casting material, various molding materials and wired sheet glass and a sealing agent for rust prevention / water proof of the glass laminate end face (cut section), autoparts, electrical machinery parts, several kinds of machine part, etc.

[0203]

[Example]Although concrete working example of this invention is combined with a comparative example and described below, this invention is not limited to following working example.

[0204]The inside of following working example and a comparative example "part", and "%", a "weight section", and "% of the weight" are expressed, respectively. In this example, "triamine" means pentamethyl diethylenetriamine.

[0205]JA "number average molecular weight" and "molecular weight distribution (ratio of weight average molecular weight to a number average molecular weight)" were computed among following working example by the standard polystyrene converting method for having used gel permeation chromatography (GPC). However, chloroform was used as what was filled up with polystyrene cross linked gel as a GPC column (shodex GPC K-804; made by Showa Denko), and a GPC solvent. (Example 1 of manufacture)

(Composition of the carboxylate which has an alkenyl group) 10-undecenoic acid (150 g, 0.814 mol) and potassium tert-butoxide (91.3 g, 0.814 mol) were added to methanol (250mL), and it stirred at 0 °C. By distilling off volatile matter content under heating under reduced pressure, the undecenoic acid potassium shown in a lower type was obtained.

$\text{CH}_2=\text{CH}-(\text{CH}_2)_8-\text{CO}_2^-\text{K}^+$  (BA semi batch polymerization-1kg)

The first copper (8.39 g, 0.0585 mol) of bromination and acetonitrile (112mL) were supplied to the glass reaction vessel of 2L under a nitrogen atmosphere, and it heated for 60 minutes at 70 °C. adding butyl acrylate (224mL, 1.56 mol), 2, and 5-dibromo diethyl adipate (17.6 g, 0.0488 mol) to this — further — it stirred for 30 minutes. Triamine (0.41mL, 1.95mmol) was added to this, and the polymerization was started. Triamine (5.66mL, 27.1mmol) was added, having sampled the reaction solution after this and pursuing a reaction, and butyl acrylate (895mL, 6.24 mol) was added over 140 minutes after [ of the reaction start ] 55 minutes. Heating was continued to the addition back pan of butyl acrylate for 170 minutes. At this time, the consumption rate of butyl acrylate was 92.9% from GC measurement. After diluting the mixture with toluene and processing it with activated alumina, the water-white polymer [1] was obtained by heating volatile matter content under decompression and distilling it off. The number average molecular weight of the obtained polymer [1] was 21000, and molecular weight distribution was 1.1.

[0206]The above-mentioned polymer [1] (0.35 kg), the above-mentioned undecenoic acid potassium (8.85g), and dimethylacetamide 350mL were added to glassware, and it heated and stirred at 70 °C under a nitrogen atmosphere for 3 hours. After removing the volatile matter content of a reaction solution under heating under reduced pressure, it diluted with toluene and filtered. Volatile matter content was distilled out of the filtrate under heating under reduced pressure, and the solution was condensed, receiving this at polymer in silicic acid aluminum (the product made from harmony chemicals, KYO word 700PEL) — 20wt% — in addition, it heated and stirred at 100 °C for 3 hours.

The alkenyl group end polymer (polymer [2]) was obtained by diluting a reaction solution with toluene, filtering it and distilling volatile matter content out of a filtrate under heating under reduced pressure. The number of the alkenyl groups introduced per one molecule of polymer by  $^1\text{H-NMR}$  measurement was 1.9.

[0207]1, 1 and 3 of a polymer [2] (350g), trimethoxysilane (15.0mL), alt.formic acid methyl (3.6mL), and zerovalent platinum, 3-tetramethyl 1, and 3-divinyl disiloxane complex were taught to 1L resisting pressure reaction vessel. However, the amount of the platinum catalyst used was made into the  $5 \times 10^{-4}$  equivalent by the mole ratio to the alkenyl group of a polymer. After carrying out the pyrogenetic reaction of the reaction mixture, the silyl group end vinyl-base polymer (polymer [P1]) was obtained by carrying out decompression distilling off of the volatile matter content of a mixture. The number average molecular weight of the obtained polymer was 26000, and molecular weight distribution was 1.2. They were 1.4 pieces when asked for the number of the silyl groups of the average introduced per one molecule of polymers by  $^1\text{H NMR}$  analysis.

[0208]To 1L resisting pressure reaction vessel, similarly A polymer [2], and trimethoxysilane, alt.formic acid methyl, And after teaching 1, 1 and 3 of zerovalent platinum, 3-tetramethyl 1, and 3-divinyl disiloxane complex and carrying out a pyrogenetic reaction enough, the silyl group end vinyl-base polymer (polymer [P2]) was obtained by carrying out decompression distilling off of the volatile matter content of a mixture. The number average molecular weight of the obtained polymer was 26000, and molecular weight distribution was 1.2. They were 2.0 pieces when asked for the number of the silyl groups of the average introduced per one molecule of polymers by  $^1\text{H NMR}$  analysis.

[0209]To 1L resisting pressure reaction vessel, similarly A polymer [2] and dimethoxymethyl hydrosilane, After teaching and carrying out the pyrogenetic reaction of 1, 1 and 3 of alt.formic acid methyl and zerovalent platinum, 3-tetramethyl 1, and the 3-divinyl disiloxane complex, the silyl group end vinyl-base polymer (polymer [P3]) was obtained by carrying out decompression distilling off of the volatile matter content of a mixture. The number average molecular weight of the obtained polymer was 26000, and molecular weight distribution was 1.2. They were 1.4 pieces when asked for the number of the silyl groups of the average introduced per one molecule of polymers by  $^1\text{H NMR}$  analysis.

(Example 2 of manufacture) CuBr (8.39 g, 0.0585 mol) was taught to the separable flask of 2L with a refluxing pipe and an agitator, and the nitrogen purge of the inside of a reaction vessel was carried out to it. Acetonitrile (112mL) was added and it stirred for 30 minutes at 70 °C among the oil bath. Butyl acrylate (224mL), 2, 5-dibromo diethyl adipate (23.4 g, 0.0650 mol), and triamine (0.500mL, 0.244mmol) were added to this, and the reaction was started. Butyl acrylate (895mL) was continuously dropped over 150 minutes, heating and stirring at 70 °C. Triamine (2.50mL, 12.0mmol) was added in the middle of dropping of butyl acrylate. From the reaction start, 1,7-octadien (288mL, 1.95 mol) and triamine (4.0mL, 0.0195 mol) were added after 310-minute progress, and it heated [for 240 minutes] and stirred at 70 °C succeeding. After diluting the reaction mixture with hexane and letting an activity alumina column pass, the alkenyl group end polymer (polymer [3]) was obtained by carrying out decompression distilling off of the volatile matter content. The number average molecular weight of the polymer [3] was 20000, and molecular weight distribution was 1.3. A polymer [3] (10 kg), potassium benzoate (34.8g), and N,N-dimethylacetic acid amide (1L) were taught to 2with refluxing pipe L separable flask, and it heated and stirred at 70 °C under the nitrogen air current for 15 hours. It diluted with toluene, after removing N,N-dimethylacetic acid amide by scale loss pressing down. A part for a solid insoluble to toluene (KBr and surplus potassium benzoate) was filtered by the activity alumina column. The polymer [4] was obtained by carrying out decompression distilling off of the volatile matter content of a filtrate.

[0210]A polymer [4] (1 kg), silicic acid aluminum (200 g, the product made from harmony chemicals, KYO word 700PEL), and toluene (1L) were taught to 2with refluxing pipe L round bottom flask, and it heated and stirred at 100 °C under the nitrogen air current for 5.5 hours. After filtration removed silicic acid aluminum, the polymer [5] was obtained by carrying out decompression distilling off of the toluene of a filtrate.

[0211]1, 1 and 3 of a polymer [5] (720g), trimethoxysilane (31.7mL), alt.formic acid methyl (8.1mL), and zerovalent platinum, 3-tetramethyl 1, and 3-divinyl disiloxane complex were taught to 1L resisting pressure reaction vessel. However, the amount of the platinum catalyst used was made into the  $5 \times 10^{-4}$  equivalent by the mole ratio to the alkenyl group of a polymer. After carrying out the

pyrogenetic reaction of the reaction mixture, the silyl group end vinyl-base polymer (polymer [P4]) was obtained by carrying out decompression distilling off of the volatile matter content of a mixture. By GPC measurement (polystyrene conversion), the number average molecular weight of the obtained polymer was 23000, and molecular weight distribution was 1.4. They were 1.7 pieces when asked for the number of the silyl groups of the average introduced per one molecule of polymers by  $^1\text{H NMR}$  analysis.

[0212]1, 1 and 3 of a polymer [5], trimethoxysilane, dimethoxymethyl hydrosilane, alt.formic acid methyl, and zerovalent platinum, 3-tetramethyl 1, and 3-divinyl disiloxane complex were similarly taught to 1L resisting pressure reaction vessel. However, the input of trimethoxysilane and dimethoxymethyl hydrosilane was set to 70 to 30 by the °C mole ratio. After carrying out the pyrogenetic reaction of the reaction mixture, the silyl group end vinyl-base polymer (polymer [P5]) was obtained by carrying out decompression distilling off of the volatile matter content of a mixture. By GPC measurement (polystyrene conversion), the number average molecular weight of the obtained polymer was 23000, and molecular weight distribution was 1.4. When asked for the number of the silyl groups of the average introduced per one molecule of polymers by  $^1\text{H NMR}$  analysis, trimethoxy groups were 1.2 pieces and dimethoxymethyl group 0.5 piece.

[0213]To 1L resisting pressure reaction vessel, similarly A polymer [5], dimethoxymethyl hydrosilane, After teaching and carrying out the pyrogenetic reaction of 1, 1 and 3 of alt.formic acid methyl and zerovalent platinum, 3-tetramethyl 1, and the 3-divinyl disiloxane complex, the silyl group end vinyl-base polymer (polymer [P6]) was obtained by carrying out decompression distilling off of the volatile matter content of a mixture. By GPC measurement (polystyrene conversion), the number average molecular weight of the obtained polymer was 23000, and molecular weight distribution was 1.4. They were 1.7 pieces when asked for the number of the silyl groups of the average introduced per one molecule of polymers by  $^1\text{H NMR}$  analysis.

(Example 3 of manufacture) CuBr (251.82 g, 1.76 mol) was taught to the flowing-back tower and 50L polymerization machine with an agitator, and the nitrogen purge of the inside of a reaction vessel was carried out to them. Acetonitrile (3360mL) was added and it stirred for 20 minutes at 68 °C. Butyl acrylate (6.80L), 2, 5-dibromo diethyl adipate (526.70 g, 1.46 mol), and triamine (12.0mL, 0.0585 mol) were added to this, and the reaction was started. Butyl acrylate (26.80L) was continuously dropped over 204 minutes, heating and stirring at 70 °C. Triamine (36.0mL, 0.176 mol) was added in the middle of dropping of butyl acrylate. From the reaction start, 1,7-octadien (8640mL, 58.5 mol) and triamine (120mL, 0.585 mol) were added after 397-minute progress, and it heated and stirred at 80 °C for 240 minutes. Triamine (80mL, 0.390 mol) was added after that, and it heated and stirred at 90 °C for 240 minutes.

[0214]After having diluted the reaction mixture with toluene, removing the insoluble copper complex using the disk centrifuge and letting an activity alumina column pass, the alkenyl group end polymer (polymer [6]) was obtained by carrying out decompression distilling off of the volatile matter content. The number average molecular weight of the polymer [6] was 24000, and molecular weight distribution was 1.21. A polymer [6] (3.0 kg), potassium acetate (24.5g), and N,N-dimethylacetic acid amide (3L) were taught to 10with refluxing pipe L separable flask, and it heated and stirred at 100 °C under the nitrogen air current for 10 hours. It diluted with toluene, after removing N,N-dimethylacetic acid amide by scale loss pressing down. A part for a solid insoluble to toluene (KBr and surplus potassium acetate) was filtered by the activity alumina column. The polymer [7] was obtained by carrying out decompression distilling off of the volatile matter content of a filtrate.

[0215]A polymer [7] (3 kg), a hydrotalcite (450 g, the product made from harmony chemicals, KYO word 500SH, KYO word 700SL), and xylene (0.6L) were taught to 10with refluxing pipe L round bottom flask, and it heated and stirred at 130 °C under the nitrogen air current for 5.0 hours. After filtration removed silicic acid aluminum, the polymer [8] was obtained by carrying out decompression distilling off of the filtrate.

[0216]1, 1 and 3 of a polymer [8] (1000g), trimethoxysilane (52mL), alt.formic acid methyl (13.3mL), and zerovalent platinum, 3-tetramethyl 1, and 3-divinyl disiloxane complex were taught to 2L reaction vessel. A platinum catalyst and trimethoxysilane were added in the middle of the reaction. The amount of 69mL and the platinum catalyst used was the sum total in total, and the amount of the trimethoxysilane used was the  $1 \times 10^{-3}$  equivalent in the mole ratio to the alkenyl group of a polymer.



After carrying out a pyrogenetic reaction, the silyl group end vinyl-base polymer (polymer [P7]) was obtained by carrying out decompression distilling off of the volatile matter content of a mixture. By GPC measurement (polystyrene conversion), the number average molecular weight of the obtained polymer was 28500, and molecular weight distribution was 1.4. They were 2.5 pieces when asked for the number of the silyl groups of the average introduced per one molecule of polymers by <sup>1</sup>H NMR analysis.

[0217] To 2L reaction vessel, similarly Polymer [8] 3-mercaptopropyltrimethoxysilane. After teaching and carrying out the pyrogenetic reaction of the 2 and 2'-azobis 2-methylbutyronitrile, the silyl group end vinyl-base polymer (polymer [P8]) was obtained by fully (unreacted 3-mercaptopropyltrimethoxysilane does not remain like) carrying out decompression distilling off of the volatile matter content of a mixture. By GPC measurement (polystyrene conversion), the number average molecular weight of the obtained polymer was 28500, and molecular weight distribution was 1.4. They were 2.8 pieces when asked for the number of the silyl groups of the average introduced per one molecule of polymers by <sup>1</sup>H NMR analysis.

[0218] 1 and 3 of a polymer [8] (1000g), dimethoxymethyl hydrosilane (45mL), altformic acid methyl (13.3mL), and zerovalent platinum, 3-tetramethyl 1, and 3-divinyl disiloxane complex were similarly taught to 2L reaction vessel. a polymer [P7] — a platinum catalyst and dimethoxymethylsilane were similarly added in the middle of the reaction. After carrying out a pyrogenetic reaction enough, the silyl group end vinyl-base polymer (polymer [P9]) was obtained by carrying out decompression distilling off of the volatile matter content of a mixture. By GPC measurement (polystyrene conversion), the number average molecular weight of the obtained polymer was 28500, and molecular weight distribution was 1.4. They were 2.5 pieces when asked for the number of the silyl groups of the average introduced per one molecule of polymers by <sup>1</sup>H NMR analysis.

(Example 4 of manufacture) Based on the method indicated in working example 2 given in JP,H11-080249,A, use hydroxyethyl 2-bromo propionate as an initiator, and the first copper of bromination and a 2,2-bipyridyl are made into a polymerization catalyst. Acrylic acid-n-butyl was polymerized and the polyacrylic acid-n-butyl (polymer [9]) which adds methacrylic acid-2-hydroxyethyl in the polymerization last stage and has a hydroxyl group at the end was obtained. By GPC measurement (polystyrene conversion), the number average molecular weight of the obtained polymer was 6100, and molecular weight distribution was 1.3.

[0219] Isocyanate propyltrimethoxysilane was added to this, the urethane-ized reaction was performed, the hydroxyl group of the end was changed into the trimethoxysilyl group, and the vinyl-base polymer (polymer [P10]) which has a trimethoxysilyl group was obtained. They were 3.3 pieces when asked for the number of the silyl groups of the average introduced per one molecule of polymers by <sup>1</sup>H NMR analysis.

(Example 5 of manufacture) After teaching CuBr (923.3 g, 6.44 mol) to the reaction vessel of 250L with an agitator and carrying out the N2 seal of the inside of a reaction vessel to it, acetonitrile (6671g) was added and it stirred for 15 minutes at 65 °. Butyl acrylate (22.0 kg), 2,5-dibromo diethyl adipate (1931.2 g, 5.36 mol), acetonitrile (3000g), and triamine (44.8mL, 214.6mmol) were added to this, and the reaction was started. Butyl acrylate (88.0 kg) was dropped continuously, heating and stirring at 80 °. Triamine (179.2mL, 859.5mmol) was added in the middle of dropping of butyl acrylate. The reaction mixture (polymerization reaction mixture [10']) containing a polymer [10] was obtained by adding 1,7-octadecan (15.847 kg) and triamine (672.0mL, 3.21 mol) after heating and stirring at 80 °. successively, and continuing heating and stirring at 80 more ° for 10 hours. The alkenyl group end polymer (polymer [10]) was obtained by carrying out decompression distilling off of the volatile matter content of a reaction mixture [10'].

[0220] To the reaction vessel of 250L with an agitator, a polymer [10] (100 kg), a methylcyclohexane (100 kg), Adsorbent (2 kg each, the product made from harmony chemicals, KYO word 500SH, KYO word 700SL) was prepared, under oxygen / nitrogen mixed gas atmosphere, it heated and stirred for 2 hours, a part for 150 ° of solids was separated, and the polymer [11] was obtained.

[0221] A polymer [11] (3.2 kg), potassium acetate (74.1g), and N,N-dimethylacetic acid amide (3.2L) were taught to 10with refluxing pipe L separable flask, and it heated and stirred at 100 ° under the nitrogen air current for 8 hours. It diluted with toluene, after removing N,N-dimethylacetic acid amide by scale loss pressing down. A part for a solid insoluble to toluene (KBr and surplus potassium

acetate) was filtered by the activity alumina column. The polymer [12] was obtained by carrying out decompression distilling off of the volatile matter content of a filtrate.

[0222] A polymer [12] (3 kg), adsorbent (1800 g, the product made from harmony chemicals, KYO word 500SH, KYO word 700SL), and xylene (1.5L) were taught to 10with refluxing pipe L separable flask, and it heated and stirred at 130 ° under the nitrogen air current for 5.0 hours. After filtration removed adsorbent, the polymer [13] was obtained by carrying out decompression distilling off of the filtrate.

[0223] 1, 1 and 3 of the polymer [13] (1300g) obtained in the example 1 of manufacture, dimethoxymethyl hydrosilane (58.5mL), altformic acid methyl (17.3mL), and zerovalent platinum, 3-tetramethyl 1, and 3-divinyl disiloxane complex were taught to 2L reaction vessel. The amount of the platinum catalyst used is 30 mg by platinum conversion to 1 kg of polymers. After carrying out a 3.5h pyrogenetic reaction, 100 ° of silyl group end vinyl-base polymers (polymer [P11]) were obtained by carrying out decompression distilling off of the volatile matter content of a mixture. By GPC measurement (polystyrene conversion), the number average molecular weight of the obtained polymer was 27000, and molecular weight distribution was 1.4. They were 1.8 pieces when asked for the number of the silyl groups of the average introduced per one molecule of polymers by <sup>1</sup>H NMR analysis.

(Example 6 of manufacture) It is CuBr (188.02 g) like the example 3 of manufacture using a flowing-back tower and 50L polymerization machine with an agitator. 1.3107 mol, acetonitrile (3226mL), butyl acrylate (9396mL), Ethyl acrylate (13060mL), acrylic acid 2-methoxy ethyl (9778mL), 2, 5-dibromo diethyl adipate (786.55g), triamine (187.76mL). Use 1,7-octadecan (6452mL) as a raw material, and the reaction mixture made to react is diluted with toluene, After letting an activity alumina column pass, the alkenyl group end copolymer (copolymercopolymer [14] of alkenyl end poly (butyl acrylate, ethyl acrylate, acrylic acid methoxy ethyl) was obtained by carrying out decompression distilling off of the volatile matter content.

[0224] A copolymer [14] (3.0 kg), potassium acetate (24.5g), and N,N-dimethylacetic acid amide (3L) were taught to 10with refluxing pipe L separable flask, and it heated and stirred at 100 ° under the nitrogen air current for 10 hours. It diluted with toluene, after removing N,N-dimethylacetic acid amide by scale loss pressing down. A part for a solid insoluble to toluene (KBr and surplus potassium acetate) was filtered by the activity alumina column. carrying out decompression distilling off of the volatile matter content of a filtrate — an alkenyl group end copolymer — (— copolymer [ of alkenyl end poly (butyl acrylate, ethyl acrylate, acrylic acid methoxy ethyl) ] : — copolymer [15] was obtained.

[0225] A copolymer [15] (3 kg), a hydratealcite (450 g, the product made from harmony chemicals, KYO word 500SH, KYO word 700SL), and xylene (0.6L) were taught to 10with refluxing pipe L round bottom flask, and it heated and stirred at 130 ° under the nitrogen air current for 5.0 hours. After filtration removed silicic acid aluminum, the copolymer [16] was obtained by carrying out decompression distilling off of the filtrate.

[0226] 1, 1 and 3 of a copolymer [16] (1000g), dimethoxymethyl hydrosilane (29.8mL), altformic acid methyl (11.7mL), and zerovalent platinum, 3-tetramethyl 1, and 3-divinyl disiloxane complex were taught to 2L reaction vessel. A platinum catalyst and dimethoxymethylsilane were added in the middle of the reaction. After carrying out a pyrogenetic reaction enough, the silyl group end vinyl system copolymer (copolymer [P12]) was obtained by carrying out decompression distilling off of the volatile matter content of a mixture. By GPC measurement (polystyrene conversion), the number average molecular weight of the obtained copolymer was 21500, and molecular weight distribution was 1.3. They were 2.3 pieces when asked for the number of the silyl groups of the average introduced per one molecule of copolymers by <sup>1</sup>H NMR analysis.

(Example 7 of manufacture) One end adds isocyanate propyltrimethoxysilane to polypropylene alcohol (made in transformation [ Commercial item new pole LB-285, Mitsubishi ]) of the number average molecular weight 1200 blocked with the butoxy group, and performs a urethane-ized reaction. The hydroxyl group of the end was changed into the trimethoxysilyl group, and the polyether system polymer (polymer [P13]) which has crosslinkable silyl groups was obtained.

(Example 8 of manufacture) Ring opening polymerization of the propylene oxide was carried out by having used allyl alcohol as the initiator, and it was considered as the polyoxypropylene monoar of one end allyloxy group content of the molecular weight 2000, and was made to react to a hydroxyl



group and the benzoyl chloride of equimolar under triethylamine existence continuously. The reaction mixture was diluted with 5-times the amount hexane, and was rinsed, except for the triethylamine hydrochloride, hexane was distilled off and one end obtained the compound whose end of another side is an allyl group with the benzoyloxy group. Next, the polyether system polymer (polymer [P14]) which changes an one end allyl group into a dimethoxymethyl silylpropyl group, and has crosslinkable silyl groups was obtained using dimethoxymethylsilane and chloroplatinic acid. The molecular weight was 2500 and viscosity was 0.7 Pa-s (23 \*\*).

(Example 9 of manufacture) Use 2-ethylhexanol as an initiator and by the method of a description to JP,H3-72527,A. Make propylene oxide react under existence of a composite metal cyanide complex catalyst, and a polyoxy polypropylene monooar is manufactured. Subsequently, after making the allyl chloride react to terminal hydroxyl groups and introducing an unsaturation group, further, trimethoxysilane was made to react and the polyether system polymer (polymer [P15]) which has crosslinkable silyl groups in one end was obtained. The number average molecular weight was 3000 and viscosity was 0.6 Pa-s (23 \*\*).

(Example 10 of manufacture) Use as an initiator the polypropylene glycol of the molecular weight 3000 which has a hydroxyl group in both ends, and by the method of a description to JP,H3-72527,A. Under existence of a composite metal cyanide complex catalyst, make propylene oxide react and it is considered as a polyoxy polypropylene monooar. After making the allyl chloride below the equivalent react to terminal hydroxyl groups and introducing an unsaturation group, further, methyl dimethoxysilane below the equivalent was made to react and the polyether system polymer (polymer [P16]) which has 1.2 or less crosslinkable silyl groups on the average was obtained. When the number average molecular weight asked for the number of the silyl groups of 8000 and the average introduced per one molecule of polymers by <sup>1</sup>H NMR analysis, it was 0.9 piece.

(Example 11 of manufacture) Use as an initiator the polypropylene glycol of the molecular weight 3000 which has a hydroxyl group in both ends, and by the method of a description to JP,H3-72527,A. Under existence of a composite metal cyanide complex catalyst, make propylene oxide react and it is considered as a polyoxy polypropylene monooar. After making the allyl chloride react to terminal hydroxyl groups and introducing an unsaturation group, further, methyl dimethoxysilane of the equivalent was made to react to an unsaturation group, and the polyether system polymer (polymer [P17]) which has crosslinkable silyl groups in a molecular terminal was obtained. When the number average molecular weight asked for the number of the silyl groups of 16000 and the average introduced per one molecule of polymers by <sup>1</sup>H NMR analysis, it was 1.6 pieces.

(Working example 1-16) To the polymer [P1-P12] 100 copy obtained in the examples 1-4 of manufacture, 150 copies of colloid calcium carbonate (Hakukens CCR: product made from Shiroishi calcium), 20 copies of heavy calcium carbonate (NANOKKUSU 25A: made by Maruo Calcium). Ten copies of titanium oxide (TIPAQUE R-820 (rutile type): made by Ishihara Sangyo). Use as a plasticizer the polymer [P13-P16] (it indicates to Table 1) obtained in the examples 7-10 of manufacture, and 50 copies, thixotropic grant agent (made in DISUPARON 6500 Kusumoto Chemicals) 2 copy, and an antiaging agent (SANORU LS-765(HALS):Sankyo make.) made in Tinuvin 213:Tiiba Specialty Chemicals — one copy each, [blend and ] After mixing enough using 3 more paint roll, blended other various additive agents and carried out coating to the sheet shaped of about 2-mm thickness using various curing catalysts, and it was made to harden at a room temperature, and finger touch estimated the pliability of the hardened material after settling the hardened material for one week at a room temperature further. The number of addition parts and evaluation result of various combination drugs and a hardening agent were shown in Table 1. O expresses with evaluation of the pliability of this invention the level good as sealant for low moduli, and the level (that is, unsuitable) whose x is too hard as sealant for low moduli. About oil bleeding, after settling the hardened material for one week under 30 \*\* x 80% of atmosphere, the surface state of the hardened material was checked by viewing and finger touch, the state (namely, good state) where oil bleeding is not seen in evaluation of the oil bleeding of this invention as for O — x expresses a BETATSUKU state (that is, poor) with oil and, in \*\*, the surface expresses these middle states, respectively. Any hardened material maintained pliability sufficient as sealant for low moduli, and oil bleeding was not seen on condition of under heat and high humidity.

(Comparative example 1) Except having used phthalic acid-2-ethylhexyl to the polymer [P3] obtained in the example 1 of manufacture instead of the polymer [P13-P16] used as a plasticizer in working

example 1-16, by the same method as working example 1-16, produce a hardened material and similarly The pliability of a hardened material, Oil bleeding was observed and evaluated. The number of addition parts and each result of various combination drugs and a hardening agent were shown in Table 1.

(Comparative example 2) Except having used phthalic acid-isodecyl to the polymer [P6] obtained in the example 2 of manufacture instead of the polymer [P13-P16] used as a plasticizer in working example 1-16, the hardened material was produced by the same method as working example 1-16, and the pliability of a hardened material and oil bleeding were observed and evaluated. The number of addition parts and each result of various combination drugs and a hardening agent were shown in Table 1. The result was shown in Table 1.

(Comparative example 3) Except not having used the polymer [P13-P16] used as a plasticizer in working example 1-16 to the polymer [P9] obtained in the example 3 of manufacture, the hardened material was produced by the same method as working example 1-16, and the pliability of a hardened material and oil bleeding were observed and evaluated. The number of addition parts and each result of various combination drugs, a hardening agent, and a hardening agent were shown in Table 1. The result was shown in Table 1.

[0227]

[Table 1]

重合体	①	②	③	④	⑤	柔軟性	材料
実施例1	P1	P13	Cat.A	—	—	—	O
実施例2	P2	P13	Cat.B	D	F	—	O
実施例3	P1/P3(1:1)	P14	Cat.B	C	—	—	O
実施例4	P4	P15	Cat.B	D	G	—	O
実施例5	P6	P15	Cat.B	E	G	H	O
実施例6	P4/P6(1:1)	P15	Cat.B	C	F	I	O
実施例7	P5/P6(1:1)	P15	Cat.B	E	—	J	O
実施例8	P4/P5/P6(1:1:1)	P13	Cat.B	—	F	J	O
実施例9	P7	P13	Cat.B	E	G	H	O
実施例10	P8	P14	Cat.A	C	G	I	O
実施例11	P9	P15	Cat.A	C	F	—	O
実施例12	P10	P15	Cat.A	D	F	—	O
実施例13	P11	P14	Cat.A	C	G	—	O
実施例14	P11	P15	Cat.A	D	F	—	O
実施例15	P11	P16	Cat.A	D	F	—	O
実施例16	P12	P16	Cat.A	C	G	—	O
比較例1	P3	DDP	Cat.A	D	F	—	O
比較例2	P6	DDP	Cat.A	—	—	—	O
比較例3	P9	—	Cat.B	—	—	—	X

Pliability: O [12-P15, DOP (dioctyl phthalate, made by Kyowa Hakko Kogyo), ] — Fitness, x — Defect (it is hard — unsuitable as sealant for low moduli) oil bleeding: good < O > \*\* > x > Defect (BETATSUKU) \*\* plasticizer: P DIDP(di-isodecyl phthalate: made by Kyowa Hakko Kogyo) \*\* curing catalyst: — Cat.A—U-220 (dibutyl tin dioctyl acetate), Two copies, Cat.B — (in octyle / lauryl amine —3 copy/1 copy) \*\* air-oxidation hardenability substance: C — Tung oil, D — linseed oil, and, [ E—1,2-polybutadiene \*\* photorealist substance: F— pentaerythritol doria ] G— trimethylolpropane-triacrylate \*\* allied compound: H — Hexamethylsilazane, I — A trimethyl siloxysilane, J — To the polymer [P11] 100 copy obtained in the example 5 of this (trimethylsilyl) ghost (working example 17-18) manufacture of trimethylolpropane, 150 copies of colloid calcium carbonate (Hakukens CCR: product made from Shiroishi calcium), 20 copies of heavy calcium carbonate (NANOKKUSU 25A: made by Maruo Calcium), ten copies of titanium oxide (TIPAQUE R-820 (rutile type): made by Ishihara Sangyo), 60 copies of plasticizers of [P15 and P14], thixotropic grant agent (made in DISUPARON 6500 Kusumoto Chemicals) 2 copy, and an antiaging agent (SANORU LS-765 (HALS):Sankyo make.) made in Tinuvin 213:Tiiba Specialty Chemicals — one copy each, [blend and ] After mixing enough with a planetary mixer, one copy each of silanol content compound (A-1120, A-171: all Nippon Unicar make) and two copies of curing catalysts (made in transformation [ U-220 (dibutyl tin diacetyl acetate): Day the east ] were added further, and 1 liquid composition was produced. The viscosity at 23 \*\* of the constituent was measured. Carried out coating to the sheet shaped of about 2 more mm thickness, it was made to harden at a room temperature, and the pliability of a hardened material and oil bleeding were observed and evaluated like working example 1-17. The number of addition parts and each result of various combination drugs and a hardening agent